HONI SOIT QUI MAL Y PENSE
DIEU ET MON DROIT

Agricultural Research Institute

PUSA

THE JOURNAL

OF THE

American Chemical Society

VOLUME XXXII

1910

Editor:

WILLIAM A. NOYES.

Associate Editors:

M. T. BOGERT,
EDWARD HART,
W. F. HILLEBRAND,
J. H. LONG,
ARTHUR A. NOYES,
CHARLES L. PARSONS,
H. P. TALBOT,
H. W. WILEY.

EASTON, PA.:
ESCHENBACH PRINTING COMPANY
1910

A. E. Vinson: The Stimulation of Premature Ripening by Chemical Means.. 208
John E. Bucher: The Acids of the Phenylpropiolic Series and Their Condensation to Naphthalene Derivatives........ 212
Julius Stieglitz: Catalysis on the Basis of Work with Imido Esters.......... 221
P. A. Levene: On the Biochemistry of Nucleic Acids.......... 231
New Books: General Inorganic Chemistry; Experimentelle Untersuchungen über Atomgewichte; Treatise on Qualitative Analysis; A Manual of Qualitative Analysis; An Introduction to Chemical Analysis for Students of Medicine, Pharmacy and Dentistry; Quantitative Chemical Analysis; Adapted for Use in the Laboratories of Colleges and Schools; Anleitung für das organisch präparative Praktikum; Kolloidchemische Beihefte; Metallographie: Ein ausführliches Lehr- und Handbuch der Konstitution und der physikalischen, chemischen und technischen Eigenschaften der Metalle und metallischen Legierungen; The Elements of Metallography........ 240
Recent Publications.... 247

March.

General, Physical and Inorganic.

F. W. Clarke: Seventeenth Annual Report of the Committee on Atomic Weights. Determinations Published during 1909.... 255
Theodore William Richardson and Richard Henry Jesse, Jr: The Heats of Combustion of the Octanes and Xylenes........ 268
Gregory Paul Baxter and Grinnell Jones: A Revision of the Atomic Weight of Phosphorus.......... 298
Frederic P. Dewey: The Solubility of Gold in Nitric Acid.......... 318
William H. Chapin: Halide Bases of Tantalum.......... 323
M. A. Hunter: Metallic Titanium.......... 330
Note: The Preparation of Platinum Black.......... 336

Organic and Biological.

C. S. Hudson: A Relation between the Chemical Constitution and the Optical Rotatory Power of the Sugar Lactones.......... 338
Frederick B. Power and Arthur H. Salway: Chemical Examination of Pumpkin Seed.......... 346
Frederick B. Power and Arthur H. Salway: Chemical Examination of Watermelon Seed.......... 360
John E. Bucher: The Constitution of Retene and Its Derivatives.......... 374
F. J. Moore: The Colored Salts of Schiff's Bases.......... 382
Edward H. Keiser and LeRoy McMaster: The Action of Magnesium upon the Vapors of Organic Compounds.... 388
R. R. Renshaw and F. C. Ware: Studies in the Action of Heat on Milk........ 391
S. L. Jodidi: Organic Nitrogenous Compounds in Peat Soils.......... 396
Review: Some Recent Advances in Organic Chemistry.......... 410
New Books: Einführung in die allgemeine und anorganische Chemie auf elementarer Grundläge: General Chemistry for Colleges.......... 426
Recent Publications.......... 428

April.

General, Physical and Inorganic.

Theodore William Richards and Laurie Lorne Burgess: The Adiabatic Determination of the Heats of Solution of Metals in Acids.......... 431

Francis G. Benedict and Harold L. Higgins: An Adiabatic Calorimeter for Use with the Calorimetric Bomb 461
Edward W. Washburn: A Simple System of Thermodynamic Chemistry Based upon a Modification of the Method of Carnot 467
George McPhail Smith: Heterogeneous Equilibria between Aqueous Metallic Solutions; the Interaction of Mixed Salt Solutions and Liquid Amalgams (First Paper). A Study of the Reaction, $KHg_m \times Na^{\cdot} \rightleftarrows K^{\cdot} \times NaHg_n \times (m-n) Hg$ 502
Theodore W. Richards and Gregory P. Baxter: Concerning the Correction of the Apparent Weight of a Salt to the Vacuum Standard 507
Grinnell Jones: The Atomic Weight of Hydrogen 513
C. James: Thulium 517
W. D. Harkins: The Marsh Test and Excess Potential 518
Ellwood B. Spear, Edward E. Wells and Brainerd Dyer: Electrolytic Determination of Zinc 530
Ellwood B. Spear. On the Causes of the High Results in the Electrolytic Determination of Zinc 533
Notes: Titration of Ferrous Salts in the Presence of Hydrochloric and Phosphoric Acids; The Action of Coke on Solutions of Ferric Chloride; Note on the Paper Entitled "Some Organic Tungstates" 539

Organic and Biological.

D. McIntosh: The Basic Properties of Oxygen Compounds of Dimethylpyrone and the Halogen Hydrides 542
Harold L. Higgins and Alice Johnson: Elementary Analysis by Means of a Calorimetric Bomb 547
Hope Sherman and H. L. Higgins: The Composition of Some Bengali Food Materials 558
M. E. Pennington and A. D. Greenlee: An Application of the Folin Method to the Determination of the Ammoniacal Nitrogen in Meat 561
M. E. Pennington and J. S. Hepburn: The Determination of the Acid Value of Crude Fat and Its Application in the Detection of Aged Foods 568
New Books: The Fundamental Principles of Chemistry: Elementary Modern Chemistry; Recent Andvaces in Physical and Inorganic Chemistry 572
Recent Publications 575

May.

General, Physical and Inorganic.

J. W. Turrentine: On the Oxalates of Hydrazine 577
E. T. Allen and John Johnston: The Exact Determination of Sulphur in Soluble Sulphates 588
H. W. Foote: On the Formation of Double Salts 618
G. McP. Smith and H. C. Bennett: Additional Notes on the Alkali and Alkali-earth Amalgams 622
Louis J. Curtman: Some New Double Arsenates 626
E. M. Chamot and D. S. Pratt: A Study of the Phenolsulphonic Acid Method for the Determination of Nitrates in Water. II. The Composition of the Yellow Compound 630
W. S. Kimley: The Mercury Cathode in Rapid Electroanalysis 637
F. J. Metzger and M. Heidelberger: The Volumetric Determination of Cerium in Cerite and Monazite 642

D. L. Randall: The Reaction between Hydriodic Acid and Bromic Acid in the Presence of a Large Amount of Hydrochloric Acid 644
Alvin S. Wheeler: Composition of Sea Waters near Beaufort, North Carolina .. 646
Charles Baskerville and Reston Stevenson: Apparatus for Drying Flasks, Etc. .. 650
Morris Loeb and S. R. Morey: Analysis of Some Bolivian Bronzes 652
Edward W. Washburn: The Fundamental Law for a General Theory of Solutions 653

Organic and Biological.

Graham Lusk: The Fate of the Amino Acids in the Organisms 671
Jerome Alexander: Some Colloid-chemical Aspects of Digection, with Ultramicroscopic Observations 680
Lawrence J. Henderson and Alexander Forbes: On the Estimation of the Intensity of Acidity and Alkalinity with Dinitrohydroquinone 687
Philip Adolph Kober: The Quantitative Distillation of Ammonia by Aeration .. 689
Louis W. Riggs: The Determination of Iodine in Protein Combinations 692
W. H. Warren: An Apparatus for Absolute Alcohol 698
Note: An Adjustable Automatic Burette 703
Review: Recent Work in Biological Chemistry 704
New Books: Einführung in die Chemie: Ein Lehrbuch für höhere Lehranstalten und zum Selbstunterricht; Introduction to Physical Chemistry; Analyse der Silikat—und Karbonat Gesteine; Das Radium und die Farben; The Simple Carbohydrates and the Glucosides; A Course in Inorganic Chemistry for Colleges; Outline of Bacteriology (Technical and Agricultural) 722
Recent Publications 726

June.

General, Physical and Inorganic.

Walter K. Van Haagen: Halides of Tantalum 729
Gilbert N. Lewis and Carl L. von Ende. The Potential of the Thallium Electrode. 732
Miles S. Sherrill: The Ionization of Salts in Mixtures with No Common Ion 741
Frank F. Rupert: The Solid Hydrates of Ammonia. II 748
Horace G. Byers and Marc Darrin: The Influence of the Magnetic Field on the Passive State of Iron 750
Robert Stewart and J. E. Greaves: The Influence of Chlorine upon the Determination of Nitric Nitrogen 756
George S Jamieson: On a New Volumetirc Method for Cobalt and Nickel 757

Organic and Biological.

Treat B. Johnson and Herbert H. Guest: Researches on Amines: Alkylations with Dimethylsulphate. Synthesis of Dimethylphenylethylamine 761
Alvin S. Wheeler and W. M. Oates: The Bromination of Anthranilic Acid 770
C. S. Hudson and H. S. Paine: The Inversion of Cane Sugar by Invertase. IV. The Influence of Acids and Alkalies on the Activity of Invertase 774
B. Herstein: Fehling's Solution: A Contribution to the History of Chemical Reagents 779
Marston Taylor Bogert: A Review of Some Recent Investigations in the Quinazoline Group 784
Richard Sydney Curtiss: The Cause of Color in Organic Compounds 795
Notes: The Instability of Alloxan; An Improved Siphon 809
New Books: Neuvième Congrès International de Géographie; Wall Charts for

Sugar Chemists; Le Cinquantenaire de l'atomecanique ou de la Mécanique des atomes; Manuel théorique et pratique d'analyse volumétrique............ 811
Recent Publications 813

July.

General, Physical and Inorganic.

Arthur A. Noyes: Quantitative Application of the Theory of Indicators to Volumetric Analysis.. 815
Gilbert N. Lewis: The Theory of the Determination of Transference Numbers by the Method of Moving Boundaries.................................. 862
Frank K. Cameron and James M. Bell: The Phosphates of Calcium. IV...... 869
C. James and L. A. Pratt: Basic Nitrate of Yttrium.................... 873
James M. Bell: The Rate of Extraction of Plant Food Constituents from the Phosphates of Calcium and from a Loam Soil 879
Notes: Red Lines for a Balance Scale; Rack for Holding Reagents in Bulk... 884

Organic and Biological.

C. S. Hudson: Is the Hydrolysis of Cane Sugar by Acids a Unimolecular Reaction when Observed with a Polariscope? 885
C. S. Hudson: A Review of Discoveries on the Mutarotation of the Sugars 889
Recent Publications 894

August.

General, Physical and Inorganic.

Alexander Smith and Alan W. C. Menzies. Studies in Vapor Pressure I. A Method for Determining under Constant Conditions the Boiling Points of Even Minute Quantities of Liquids and of Non-Fusing Solids.......... 897
Alexander Smith and Alan W. C. Menzies: A Common Thermometric Error in the Determination of Boiling Points under Reduced Pressure 905
Alexander Smith and Alan W. C. Menzies: Studies in Vapor Pressure: II. A Simple Dynamic Method, Applicable to Both Solids and Liquids, for Determining Vapor Pressures and also Boiling Points at Standard Pressures...... 907
W. C. Bray and G. M. J. MacKay: The Conductance and Ionization of Potassium Triiodide, and the Equilibrium between Iodine, Iodide, and Polyiodides in Aqueous Solution.. 914
W. C. Bray: The Hydrolysis of Iodide and of Bromine....................... 932
John Johnston: The Thermal Dissociation of Calcium Carbonate............ 938
W. H. Sloan: On the Conductivity of Some Concentrated Aqueous Solutions at Zero.. 946
J. A. Fries: Electric Combustion Furnace for Methane Determination 949
O. F. Tower: The Precipitation of the Iron Group and the Composition of Certain Ferric Formates.. 953
O. L. Barnebey and R. M. Isham: A Rapid and Accurate Method for the Determination of Titanium... 957
Otis D. Swett: Apparatus for the Determination of Arsenic.................. 962
M. R. Schmidt: A Colorimetric Determination of Manganese in the Presence of Iron.. 965
Notes: The Chemical Laboratory of the University of Washington; A Modified Burette for Standard Alkali Solutions; The Purification of Mercury; On the Preparation of a Cuprous Nitrate, $CuNO_3.2NH_3$.......................... 967

Organic and Biological.

Stroud Jordan: The Condensation of Some Primary Aromatic Amines with Chloral-Aniline 973
Herman Schreiber: The Determination of Total Sulphur in Organic Matter... 977
C. S. Hudson and H. S. Paine: The Inversion of Cane Sugar by Invertase. V. The Destruction of Invertase by Acids, Alkalies and Hot Water.......... 985
Arthur Michael: Outline of a Theory of Organic Chemistry Founded on the Law of Entropy..... 990
New Books: The Elements of the Science of Nutrition..... 1007
Recent Publications..... 1008

September.

General, Physical and Inorganic.

A. A. Noyes and K. G. Falk: The Properties of Salt Solutions in Relation to the Ionic Theory. I. Mol-numbers Derived from the Freezing-point Lowering. 1011
Hippolyte Gruener: Silver Nitrate Formed by the Action of Nitric Acid on Silver Sulphide..... 1030
Clifford Richardson: Grahamite, a Solid Native Bitumen..... 1032

Organic and Biological.

S. P. Mulliken: Progress in Systematic Qualitative Organic Analysis.......... 1049
William A. Noyes and L. P. Kyriakides: Synthesis of the α,α'-Dimethyladipic Acids, and Separation of the Racemic Acid into Optical Isomers.......... 1057
William A. Noyes and C. G. Derick: Molecular Rearrangements in the Camphor Series. III. Oxidation Products of *l*- and *d*-Laurolene..... 1061
William A. Noyes and L. P. Kyriakides. Molecular Rearrangements in the Camphor Series. IV. Synthesis of Laurolene..... 1064
William A. Noyes: Molecular Rearrangements in the Camphor Series. V. Mechanism of the Reactions by which Laurolene is Formed..... 1068
Augustus H. Gill and Laurence R. Forrest: The Hydrocarbons of the Wool Grease Oleins. First Paper..... 1071
H. C. Sherman, E. C. Kendall and E. D. Clark: Studies on Amylases. I. An Examination of Methods for the Determination of Diastatic Power........ 1073
E. C. Kendall and H. C. Sherman: Studies on Amylases. II. A Study of the Action of Pancreatic Amylase..... 1087
Note: Preparation of *ortho*- and *para*-Nitrophenols..... 1105
New Books: Radiochemistry; Outline of Organic Chemistry; Handbuch der landwirtschaftlichen Bakteriologie; Laboratory Exercises in General Chemistry..... 1106
Recent Publications..... 1110

October.

General, Physical and Inorganic.

Annual Report of the International Committee on Atomic Weights. 1911.... 1113
C. W. Easley: The Atomic Weight of Mercury..... 1117
Clarence W. Balke: The Atomic Weight of Tantalum..... 1127
A. A. Noyes and M. A. Stewart: The Ionization Relations of Sulphuric Acid... 1133
J. E. Mills and Duncan MacRae: On Surface Energy and Surface Tension...... 1162
Theodore W. Richards, Allen W. Rowe and L. L. Burgess: The Adiabatic Determination of Heats of Solution of Metals in Acids..... 1176
Arthur E. Hill: The Inconstancy of the Solubility Product..... 1186

W. C. Bray and G. M. J. MacKay: A Volumetric Method of Determining Iodide in the Presence of Chloride, Bromide, or Free Iodine 1193
W. C. Bray: A Source of Error in Permanganate Titrations; Preliminary Note . 1204
W. C. Bray and G. M. J. MacKay: The Equilibrium between Solid Cuprous Iodide and Aqueous Solutions Containing Cupric Salt and Iodine 1207
Arthur B. Lamb: The Potential of Iron Calculated from Equilibria Measurements 1214
C. S. Hudson: The Inversion of Cane Sugar by Invertase. VI. A Theory of the Influence of Acids and Alkalis on the Activity of Invertase 1220
Ben L. Glascock: Metallic Strontium 1222
R. C. Benner: The Rapid Determination of Copper, Silver, Cadmium and Bismuth by Means of the Mercury Cathode and Stationary Anode 1231
A. T. Davenport: The Estimation of Small Quantities of Nitrogen by Pelouze's Reaction 1237
LeRoy W. McCay: The Analysis of Tin-Antimony Alloys 1241
Lily G. Kollock and Edgar F. Smith: The Determination of Indium with the Use of a Mercury Cathode 1248
F. J. Metzger and Robert F. McCrackan: A New Volumetric Method for the Determination of Manganese 1250
Mary E. Holmes and Mary V. Dover: The Use of Organic Electrolytes in Cadmium Separation 1251
Edward Bartow and B. H. Harrison: Determination of Ammonia Nitrogen in Water in the Presence of Hydrogen Sulphide 1256
William Foster: The Composition of Some Greek Vases 1259
W. C. Blasdale and W. Cruess: Conditions Affecting the Electrolytic Determination of Copper 1264
Note: New Normal Solution and Reagent Bottle 1277

Organic and Giological.

Treat B. Johnson and Herbert H. Guest: Metathetical Reactions: Ether-thioureas and their Relation to Pseudoammonium Bases 1279
Alfred N. Cook: Phenyl Ether and Some of Its Derivatives 1285
Catherine V. Gortner and Ross Aiken Gortner: The Stereomeric Azobenzenes . . 1294
Marston Taylor Bogert, Carl Gustave Amend and Victor John Chambers: Researches on Quinazolines (Twenty-fifth Paper). The Synthesis of 6- and 7-Amino-2-methyl-4-quinazolones from 4- and 5-Acetaminoacetanthranils . . 1297
R. J. Manning: Ethyl Tannate 1312
J. Bishop Tingle and S. J. Bates: Action of Amines on Phthalic Acid. VII . . . 1319
D. McIntosh: The Basic Properties of Oxygen: Compounds with Bromine and Iodine 1330
C. G. Derick: Molecular Rearrangements of Carbon Compounds 1333
C. S. Hudson and H. S. Paine: The Inversion of Cane Sugar by Invertase. VII. The Effect of Alcohol on Invertase 1350
Arthur W. Dox: The Catalase of Molds 1357
Note: The Instability of Alloxan 1362
New Books: Notions fondamentales de chimie organique 1362
Recent Publications 1362

November.

General, Physical and Inorganic.

Charles L. Parsons and H. P. Corliss: Equilibrium in the System: Potassium Iodide, Iodine and Aqueous Alcohol 1367

Charles L. Parsons and W. W. Evans: Diffusion Phenomena of the Alums.... 1378
C. L. Parsons and H. P. Corson: The Solubility of Barium Nitrate and Barium Hydroxide in the Presence of Each Other 1383
C. L. Parsons and C. L. Perkins: The Solubility of Strontium Nitrate and Strontium Hydroxide in the Presence of Each Other.... 1387
William Edward Barlow: The Binary and Ternary Alloys of Cadmium, Bismuth and Lead 1390
Alexander Smith and Alan W. C. Menzies: Studies in Vapor Pressure: III. A Static Method for Determining the Vapor Pressures of Solids and Liquids . 1412
Alexander Smith and Alan W. C. Menzies. Studies in Vapor Pressure: IV. A Redetermination of the Vapor Pressures of Mercury from 250° to 435°..... 1434
Alexander Smith and Alan W. C. Menzies. Studies in the Vapor Pressure: V. A Dynamic Method for Measuring Vapor Pressures, with its Application to Benzene and Ammonium Chloride. 1448
Gilbert N. Lewis and Charles A. Kraus: The Potential of the Sodium Electrode. 1459
Jacob S. Goldbaum and Edgar F. Smith. The Electrolytic Determination of Chlorine in Hydrochloric Acid with the Use of a Silver Anode and a Mercury Cathode 1468
Irving H. Buckminster and Edgar F. Smith: Electrolytic Separations . . . 1471

Organic and Biological

Henry A. Torrey and E. J. Cardarelli: Some Derivatives of 2-Acetyl-Naphthol-1. 1477
Henry A. Torrey and H. R. Raisky: 1-Benzoylphenyl-3-Methyl-5-Pyrazolone . 1489
Henry A. Torrey and J. B. Sumner: Note on Some Properties of Piperonyloin 1492
Marston Taylor Bogert and Louis Elsberg Wise: Some Derivatives of *p*-Aminobenzonitrile 1494
J. Bishop Tingle and S. J. Bates: Derivatives of Camphoroxalic Acid. XIII. . 1499
George Peirce: The Deviation of Ferment Action from the Monomolecular Law with Especial Reference to the Esterases 1517
Note: Extraction Apparatus 1533
New Books: Leitfaden für den Unterricht in der anorganischen Chemie didaktisch bearbeitet; Physical Chemistry for the Electrical Engineers, Principles of Chemical Geology; Beitrage zu einer Kolloidchemie des Lebens 1534
Recent Publications.. 1536

December.

General and Physical.

Alexander Smith and Alan W. C. Menzies: Studies in Vapor Pressure, VI: A Quantitative Study of the Constitution of Calomel Vapor. 1541
K. George Falk: Transference Experiments with Thallous Sulphate and Lead Nitrate. 1555
Josiah Simpson Hughes and James R. Withrow: The Character of Silver Deposits from Various Electrolytes.... 1571
G. A. Abbott: Rate of Hydration of Pyrophosphoric Acid. A Correction..... 1576
Theodore W. Richards and Otto Hönigschmid: A Revision of the Atomic Weight of Calcium. I Analysis of Calcium Bromide.... 1577
Gregory Paul Baxter: A Revision of the Atomic Weights of Silver and Iodine. 1591
D. J. McAdam, Jr.: The Atomic Weight of Vanadium.... 1603
Alan W. C. Menzies: A Method for Determining the Molecular Weights of Dissolved Substances by Measurement of Lowering of Vapor Pressure...... 1615

Alan W. C. Menzies: A Convenient Form of Apparatus for the Measurement of the Vapor Densities of Easily Volatil Substances 1624
R. C. Benner and M. L. Hartmann: Rapid Determinations and Separations by means of the Mercury Cathode and Stationary Anode 1628
Corrections to Papers by E. W. Washburn. 1636

Organic and Biological.

K. George Falk and J. M. Nelson: The Electron Conception of Valence. 1637
Marston Taylor Bogert, George Denton Beal, and Carl Gustave Amend: Researches on Quinazolines (Twenty-Sixth Paper). The Synthesis of Some Stilbazoles, Hydrazones and Schiff Bases in the 4-Quinazolone Group. 1654
William A. Noyes and A. W. Homberger: Molecular Rearrangements in the Camphor Series. VI. Isocampholactone 1665
William A. Noyes and Luther Knight: Molecular Rearrangements in the Camphor Series. VII. Derivatives of Isocamphoric Acid, *r*-Dihydrohydroxycampholytic Acid. 1669
Oswald Schreiner and Edmund C Shorey: Some Acid Constituents of Soil Humus. 1674
Edmund C. Shorey and Elbert C Lathrop: Pentosans in Soils. 1680
Paul E. Howe, T. A. Rutherford and P B. Hawk: On the Preservation of Feces 1683
S. A. Rulon, Jr., and P. B. Hawk: Studies on Water Drinking. III. On the Uric Acid Elimination following Copious Water Drinking between Meals. . . 1686
Note: A Convenient Potash Bulb 1691
New Books: A Manual of Volumetric Analysis, History of Chemistry, Neuere Anschaungen auf dem Gebiete der anorganischen Chemie; Die Alkaloide. . . 1693
Recent Publications 1698
Index. 1700

VOL. XXXII. JANUARY, 1909. NO. 1.

THE JOURNAL

OF THE

American Chemical Society

REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1910.

Received October 25, 1909.

Since the preparation of our last report there has been much activity in the determination of atomic weights. A brief summary of the results obtained is as follows:

Chlorine.—A novel comparison of chlorine with oxygen is due to Guye and Fluss.[1] Nitrosyl chloride, NOCl, was first weighed, and then distilled over silver, to absorb chlorine, then over heated copper, to absorb oxygen, and finally over metallic calcium, which retained the nitrogen. The complete analysis of the chloride was thus effected. From the direct weights of the oxygen and chlorine, Cl = 35.468.

Nitrogen.—In the investigation just cited, Guye and Fluss give data which correspond to N = 14.006. Guye and Pintza[2] determined the density of the mixed gases produced by the decomposition of ammonia, and so measured its composition by volume. If H = 1.0076, then N = 14.014. The authors regard the determination as having only a significance corroborative of the lower value for nitrogen.

The ratio AgCl : NH_4Cl : : 100 : 37.3217 has been measured by Richards, Koethner and Tiede.[3] Reduced with Ag = 107.881, Cl = 35.4574, and H = 1.0076, N = 14.0085. If H = 1.0078, N = 14.008. The values assigned to silver and chlorine are derived from former researches by Richards and his colleagues in the Harvard laboratory.

Carbon.—From the ratio between silver and tetraethylammonium bromide, as measured by Scott,[4] C = 12.017 when Ag = 107.88. A single experiment with the corresponding methyl compound gave C = 12.019. These values are too high to be accepted until they have been confirmed by other methods.

---

[1] *J. chim. phys.*, **6**, 732.

[2] *Compt. rend.*, **147**, 925.

[3] THIS JOURNAL, **31**, 6.

[4] *J. Chem. Soc.*, **95**, 1200.

From the density of methane, Baumé and Perrot[1] find C = 12.004. From the density of toluene, as determined by Ramsay and Steele, Leduc[2] computes C = 12.003.

Iodine and Silver.—Baxter and Tilley[3] have determined the ratio between iodine pentoxide and silver. The pentoxide was reduced by means of hydrazine, and the hydriodic acid so produced was balanced in the usual way against silver. From the ratio thus found, $I_2O_5 : 2Ag :: 100 : 64.6225$, and 64.6230 (two series), combined with the ratio I : Ag :: 100 : 84.8843, the authors find that the atomic weight of Ag lies between 107.847 and 107.850. The corresponding value for iodine is I = 126.891.

Phosphorus.—From the density of phosphine, PH_3, Ter Gazarian[4] finds P = 30.906.

Arsenic.—Atomic weight redetermined by Baxter and Coffin.[5] The ratios $Ag_3AsO_4 : 3AgCl$ and $Ag_3AsO_4 : 3AgBr$ were determined by two methods: one by solution and precipitation in the usual way, the other by heating the arsenate in a stream of hydrochloric or hydrobromic acid. The final, mean result is As = 74.957, when Ag = 107.880.

Chromium.—From analyses of silver chromate, by two methods, Baxter, Mueller and Hines[6] find Cr = 52.008 when Ag = 107.88. With similar analyses of silver dichromate, Baxter and Jesse[7] find Cr = 52.013. The mean value is 52.01.

Tellurium.—Lenher[8] converted the double bromide K_2TeBr_6 into 2KCl by heating, first in a stream of chlorine, and afterwards in hydrochloric acid. Sixteen very concordant experiments were made, giving the molecular ratio between the two compounds. The final mean value is Te = 127.55.

Mercury.—Analyses of mercuric chloride have been made by Easley,[9] who determined the proportion of mercury in the compound, and also the ratio $HgCl_2 : 2AgCl$. By the first method, Hg = 200.48; by the second method Hg = 200.62. These values are surprisingly high, but as Easley is to continue his investigation it would be unwise to accept them until his work is all done. It is quite possible that the increase may be ultimately verified.

---

[1] *Compt. rend.*, **148**, 39.

[2] *Ibid.*, **148**, 832.

[3] THIS JOURNAL, **31**, 201.

[4] *Compt. rend.*, **148**, 1397.

[5] THIS JOURNAL, **31**, 297.

[6] *Ibid.*, **31**, 529.

[7] *Ibid.*, **31**, 541.

[8] *Ibid.*, **31**, 20.

[9] *Ibid.*, **31**, 1207.

Palladium.—Atomic weight determined by Gutbier, Haas and Gebhardt,[1] by analyses of palladosamine bromide. The final, most probable mean value, when $N_2H_6Br_2$ = 193.908, is Pd = 106.689.

International Atomic Weights, 1910.

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.9	Neon	Ne	20.0
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.0
Caesium	Cs	132.81	Platinum	Pt	195.0
Calcium	Ca	40.09	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.6
Cerium	Ce	140.25	Radium	Ra	226.4
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.5	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.4	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.62
Gallium	Ga	69.9	Sulphur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.0
Glucinum	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	4.0	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.42
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.85	Tungsten	W	184.0
Krypton	Kr	83.0	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.2
Lead	Pb	207.10	Xenon	Xe	130.7
Lithium	Li	7.00	Ytterbium		
Lutecium	Lu	174.0	(Neoytterbium)	Yb	172.0
Magnesium	Mg	24.32	Yttrium	Yt	89.0
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.0	Zirconium	Zr	90.6

---

[1] *J. prakt. Chem.* [2], 79, 457. This includes the work of Haas, cited in the report for 1909.

Krypton and Xenon.—Moore[1] isolated krypton and xenon in considerable quantities from the residues from 120 tons of liquid air. Calculated from the densities of the two gases the atomic weights are Kr = 83.012, and Xe = 130.70.

It will be seen from the evidence given above that few changes are needed in the table of atomic weights. Chromium, 52.01, may be rounded off to 52, as compared with the 52.1 formerly accepted. Arsenic becomes 74.96, in accordance with the work of Baxter and Coffin. The new values for krypton and xenon should also be adopted. As regards mercury, action may be deferred until more evidence is received.

Signed, F. W. CLARKE,
T. E. THORPE,
W. OSTWALD,
G. URBAIN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

FURTHER INVESTIGATION CONCERNING THE ATOMIC WEIGHTS OF SILVER, LITHIUM AND CHLORINE.

BY THEODORE W. RICHARDS AND HOBART HURD WILLARD.

Received October 28, 1909.

PART I.—THE RATIO OF LITHIUM CHLORIDE TO SILVER CHLORIDE AND SILVER.

Introduction.

The present uncertainty in the atomic weight of silver causes confusion and uncertainty throughout the whole table of atomic weights. Long ago Dumas[2] pointed out that Stas, with all his care, had not succeeded in preparing pure silver, and accordingly that the atomic weights referred to silver need revision. Later, in reply to Dumas, Stas[3] sought to determine the oxygen remaining in the metal and succeeded in finding only a trace. Hence for many years Dumas' criticism was unheeded. A careful study of Stas's experiments shows, however, that the metal which he used in these later trials had not been treated in the same way as that which he used in his work upon atomic weights and hence that the presence or absence of oxygen in the later samples proved little with regard to the earlier samples. As a matter of fact it was shown in 1903 in the chemical laboratory of Harvard University[4] that Stas's silver must have been impure to the extent of at least 0.015 per cent. and that therefore his value for the atomic weight of this element, as well as of the others which had been referred to it, must have been in error. Clearly Stas's value for silver must be too large, but no attempt was made at that time to discover just how great the error might be, this proof being a somewhat complicated matter. Since that time increasing evidence has been presented, especially by Guye, tending to show that the discrepancy is serious. Because most other elements are referred to oxygen only through silver, on account of the insolubility of many silver salts and their consequent ease of precipitation, this uncertainty in the atomic weight of silver is one of very serious moment. Indeed a majority of the atomic weights cannot be referred to oxygen with precision until the relation between silver and oxygen is ascertained without doubt.[1]

---

[1] *J. Chem. Soc.*, 93, 2181.

[2] Dumas, *Ann. chim. phys.*, 14, 289 (1878).

[3] Stas, *Oeuvres Complètes*, III, 106–125 (Brussels, 1903).

[4] Richards and Wells, "A Revision of the Atomic Weights of Sodium and Chlorine," Carnegie Institution of Washington, Publication No. 28; THIS JOURNAL, 27, 459 (1905); *Z. anorg. Chem.*, 47, 56 (1905). This paper is reprinted in full in "Experimentelle Untersuchungen über die Atomgewichte," by T. W. Richards, page 689 (Hamburg, 1909), and also in *Chem. News*, 93.

To discover the most suitable method of attaining this end, and to obtain the greatest accuracy possible in the solution of the problem, was the object of the present research. We were fortunate in being able to profit by previous experience, many of the difficulties having already been surmounted in previous investigations carried out in this laboratory.

Before discussing the present investigation, it will be helpful to review briefly the work previously done relating to the oxygen-silver ratio. Unfortunately no compound of silver and oxygen exists of a nature suitable for exact work. The two common oxides of silver are far too unstable to yield results possessing any precision, and moreover, the amount of oxygen in even the higher of these oxides is a comparatively small percentage of the whole. Hence the necessary errors of the determination are greatly magnified in the calculation. For this reason it is necessary, as Stas realized, to study a compound of silver and oxygen which contains some third element, and various salts are available for the purpose. Stas himself used chiefly the chlorates, bromates, and iodates for this purpose, determining the ratio $3O : Ag$ by multiplying together the values found by him for the following pairs of ratios, thus:

$$\frac{3O}{KCl}\cdot\frac{KCl}{Ag}=\frac{3O}{Ag};\quad \frac{3O}{AgCl}\cdot\frac{AgCl}{Ag}=\frac{3O}{Ag};\quad \frac{3O}{AgBr}\cdot\frac{AgBr}{Ag}=\frac{3O}{Ag};\quad \frac{3O}{AgI}\cdot\frac{AgI}{Ag}=\frac{3O}{Ag}.$$

In each case the first ratio was obtained by the decomposition of a halate (*i. e.*, a chlorate, bromate, or iodate) and the second ratio by the comparison of silver with a halide. If the exact identity of the halide obtained from each oxygen salt with that employed in the corresponding second process could be proved, and if the various substances had been pure, the method would have been an admirable one; but unfortunately neither of these important qualifications was completely attained. Moreover, other minor errors crept into the work.[1]

---

[1] "Report International Committee on Atomic Weights, 1906," Guye and Ter Gazarian, *Compt. rend.*, 143, 411 (1906). Noyes, THIS JOURNAL, 29, 1719 (1907).

The nitrate and sulphate of silver were also studied by Stas, and his figures concerning these substances may be used in a similar way. These researches have been recently repeated with greater precision in this laboratory,[2] but here the outcome is complicated by the fact that the relation neither of nitrogen to silver nor of sulphur to silver is precisely known. Nitrogen, it is true, has been referred with much plausibility to oxygen, with the help of gas densities; but this is a physical rather than a chemical method of determining atomic weights. Excellent though it undoubtedly is as corroborative evidence, it cannot carry with it the conclusiveness which a chemical determination could furnish. On the other hand, the atomic weight of sulphur is far from certain.

Without attempting to give a complete historical discussion, the most important results of other investigations may be mentioned. The interesting and valuable results of Dixon and Edgar,[3] of W. A. Noyes[4] and H. C. P. Weber and of Edgar alone[5] upon the quantitative synthesis of hydrochloric acid furnish less direct evidence upon the matter in hand, for they need the introduction of two other ratios, namely, that of hydrogen to oxygen and that of chlorine to silver, in order to solve the problem. Thus:

$$\frac{2\mathrm{H}}{2\mathrm{Cl}} \cdot \frac{2\mathrm{C}}{2\mathrm{Ag}} \cdot \frac{\mathrm{O}}{2\mathrm{H}} = \frac{\mathrm{O}}{2\mathrm{Ag}}.$$

Even if the result were not burdened with all the errors which may reside in the additional figures, it would not be very satisfactory, because oxygen is compared with over thirteen times its weight of silver, and any error becomes greatly magnified in the calculation.

Simpler arithmetical manipulation is demanded by the recent interesting complete analysis by Guye and Fluss[6] of nitrosyl chloride, NOCl, but the result is still somewhat open to the last objection. Thus:

$$\frac{\mathrm{O}}{\mathrm{Cl}} \cdot \frac{\mathrm{Cl}}{\mathrm{Ag}} = \frac{\mathrm{O}}{\mathrm{Ag}}.$$

Here the weight of oxygen for a given weight of silver is double that in the last case.

A more promising method has been developed by Baxter,[7] and carried out with the assistance of G. S. Tilley, namely, the direct analysis by decomposition of iodine pentoxide. In this way may be determined with considerable accuracy the ratio $I_2 : 5O$ and by multiplying the results by the ratio of silver to iodine,[1] the ratio of $2Ag : 5O$ is at once obtained. Thus:

---

[1] The best discussion of this subject is to be found in Brauner's admirable discussion on "The Fundamental Atomic Weights" in Abegg's "Handbuch der anorganischen Chemie," II, 1, 177–182.

[2] *Publ. Carnegie Inst., Washington,* 69.

[3] *Phil. Trans.,* 205, 169.

[4] THIS JOURNAL, 30, 13 (1908).

[5] *Proc. Roy. Soc., London* (*A*) 81, 216 (1908).

[6] Guye and Fluss, *J. chim. phys.,* 6, 732 (1908).

[7] Baxter and Tilley, THIS JOURNAL, 31, 201 (1909).

$$\frac{5O}{2I} \cdot \frac{2I}{2Ag} = \frac{5O}{2Ag}.$$

If the second ratio were known with the greatest accuracy, this method would be an excellent one, but the peculiar nature of silver iodide has interfered with the attainment of quite as certain results concerning this substance as concerning the other silver halides.

The values obtained for silver from these various methods range from 107.92, based upon Edgar's value for chlorine and Morley's value for hydrogen, to 107.85, based upon Baxter and Tilley's work with iodine pentoxide, and it is safe to conclude that the truth lies between these extremes. Nevertheless, the range of uncertainty (0.07, or distinctly over one-twentieth of one per cent.) is far too great for a datum of such importance.

The necessity for further work upon the ratio of silver to oxygen is very evident, and the present paper recounts an extended investigation, protracted over two years, which has furnished entirely new results of a nature apparently more trustworthy than any that had gone before.

As a first step, all substances which might possibly be available for obtaining further knowledge of this very important ratio were scrutinized with the greatest care, in order to determine whether or not a better starting-point might be found. Evidently, from the foregoing remarks, the selection of the substance for this purpose depends upon more than one consideration. In the first place, it is important that the actual weights of the two elements to be compared should not be very different, so that the error in one may not be greatly magnified in a calculation of the other; hence, because the atomic weight of oxygen is much smaller than that of silver, the comparison must involve several atoms of oxygen with one of silver, if possible. For this reason the most highly oxygenated salts were studied first. It is, moreover, necessary to choose a salt of such a nature that the two ratios $\frac{MXO_y}{MX}$ and $\frac{MX}{Ag}$ may each be accurately determined. With respect to each requirement, the perchlorates seemed to furnish a peculiarly suitable starting-point. It is indeed remarkable that all previous investigators have chosen to work with chlorates in preference to the perchlorates, which are more stable, contain more oxygen, and are more easily obtained pure.

---

[1] Baxter, *Proc. Am. Acad.*, 41, 73 (1905).

The choice among the perchlorates was determined by the other considerations which must always form an important factor in a choice of this kind, namely, the nature of the substances to be weighed. In order that accurate results may be obtained, it is obvious that all the substances whose precise weights come into consideration should be capable of complete purification and thorough drying, and the great difficulties attending these processes are governed largely by the specific nature of the substances. In order that a substance may be prepared in a pure state, it must be capable of easy crystallization in such a way as to free it from its usually attendant impurities; and in order that it may be dried, it must be capable of fusion without decomposition. There are no perbromates and the periodates are too unstable; among the perchlorates the only substance which corresponds to these specifications seems to be lithium perchlorate, which fuses at 236° and loses no oxygen at 300°. Fortunately in other respects this substance is peculiarly well suited for the purpose. Its decomposition products, if any, can be accurately determined. It crystallizes well, and its solubility has a large temperature coefficient; therefore it may be easily prepared pure. It is not deliquescent or markedly hygroscopic in fairly dry air. It can be synthesized from the chloride merely by the evaporation of this salt with a slight excess of perchloric acid, the less volatile perchloric acid easily expelling the more volatile hydrochloric acid. Finally it contains over 60 per cent. of oxygen—probably more available oxygen than any other known compound, not excepting anhydrous hydrogen peroxide. Ten cubic centimeters of the salt, weighing about 24 grams, contain enough oxygen to occupy, under normal conditions, nearly 10 liters, and all this oxygen is lost when the salt is converted into chloride. Lithium has the least atomic weight of any metal, and chlorine the least of any halogen which forms oxygen salts; therefore it is easy to see how this favorable circumstance comes to pass. Such a substance affords a far more satisfactory means of weighing a gas than any attempt to weigh it in an uncombined condition. When one considers the bulky apparatus necessary in weighing gases, with the attendant errors, and the unavoidable small weights of gas, it is easy to see the superiority of a process involving a solid salt, containing the gas in an exceedingly condensed form. The weighing of hydrogen absorbed by palladium, a method employed in the recent work on the synthesis of water, is an illustration of this point. In the present case, we may consider the lithium chloride as absorbing oxygen, but far more efficiently.

Lithium perchlorate was finally chosen, however, only after a careful study of the other perchlorates, in order to make certain that none of the others offered other advantages outweighing those peculiar to itself. Attention was first directed toward silver perchlorate, which is easily prepared by evaporating a solution of the nitrate with excess of perchloric acid, and expelling the free acid by heat. The salt is extremely deliquescent, and is difficult to dry without slight decomposition. Its fusing point is so high (486°) that it cannot be completely fused before violent decomposition begins, and for the same reason an accurate determination of the water remaining in the salt dried at a lower temperature, would be difficult, if not impossible. Silver perchlorate was, therefore, abandoned, although it has one great advantage—it is easily converted into chloride in a current of dry hydrochloric acid gas even at ordinary temperatures, the process involving no transfer of material. The reaction is not a reduction, anhydrous perchloric acid being formed.

The alkaline perchlorates were next investigated. Potassium perchlorate cannot be fused without rapid decomposition. Sodium perchlorate has a lower fusing point (482°), but it decomposes slowly at this temperature, and hence cannot be accurately weighed. All indications therefore pointed to lithium perchlorate, whose virtues have been already described.

The ratio of silver to oxygen cannot be determined from this salt, however, until that of lithium chloride to silver is known. Thus, writing the relation in a manner analogous to that employed in the case of the chlorates:

$$\frac{4O}{LiCl} \cdot \frac{LiCl}{Ag} = \frac{4O}{Ag}.$$

Our knowledge of this second ratio (LiCl : Ag) depended upon the doubtful work of Stas, and this was at best freighted with the known errors entering into this work upon potassium and sodium chlorides. Hence, an essential step in the new work was the determination of this ratio, and incidentally of the true atomic weight of lithium. Even if Stas's value for lithium had been precise, however, instead of as we found it, nearly a whole per cent. in error, there would still have been good reason for making this determination anew with the same material used in our work with the perchlorate ratio. If the same sample of lithium chloride is used in determining both ratios, it is evident that the value obtained for the oxygen-silver ratio is independent of any other atomic weight, and that the weight of the alkaline chloride is eliminated. It matters not whether this chloride is free from other alkaline metals or contains them. To use an impure lithium salt would be, of course, a waste of time; from such a substance the atomic weight of lithium could not simultaneously be found.

The methods of determining these two ratios $\frac{LiCl}{Ag}$ and $\frac{4O}{LiCl}$, are so widely different that they will be treated separately. While the ratio of silver to a chloride has so frequently been carried out in this laboratory that the operation presents no difficulties, the method for determining the amount of oxygen in the perchlorate was solved only after a long and careful research. The former of the two processes naturally precedes the latter; accordingly the determination of the equivalent of lithium chloride, referred both to silver and to silver chloride will be found in the first section of this paper. On the other hand the second section of the paper deals with the preparation of the perchlorate and the determination of the oxygen which it contains.

We take pleasure in expressing our obligation to the Carnegie Institution of Washington for generous pecuniary assistance throughout the course of the work.

History of the Revisions of the Atomic Weight of Lithium.

A glance at the following table, which shows the results so far obtained, reveals wide discrepancies.[1]

				Atomic weight.	
	Name.	Year.		Ag = 107.93.	Ag = 107.88.
1.	Arfvedson	1817	$LiCl . AgCl$	10.1	....
2.	Vauquelin	1818	$Li_2SO_4 \cdot BaSO_4$	9.3	...
3.	Gmelin	1819	Analysis of Li_2CO_3	9.6	....
			Analysis of Li_2SO_4	10.7	....
			Gmelin assumes	7.65	...
4.	Kralovansky	1827	$Li_2SO_4 : BaSO_4$	10.1	....
5.	Hermann	1829	$Li_2CO_3 : CO_2$	6.1	....
			$Li_2SO_4 . BaSO_4$	6.1	..
6.	Berzelius	1829	$Li_2SO_4 : BaSO_4$	6.69	....
7.	Hagen	1839	$Li_2SO_4 : BaSO_4$	6.6	...
8.	Mallet	1856	$LiCl : AgCl$	6.96	6.96*
			$LiCl : Ag$	6.92	6.92*
9.	Troost	1857	Li_2CO_3 preliminary value	6.5	....
10.	Mallet	1859	$Li_2SO_4 : BaCl_2$	7.01	....
11.	Diehl	1862	$Li_2SO_4 \cdot BaSO_4$	7.04	....
			$Li_2CO_3 : CO_2$	7.03	7.03*
12.	Troost	1862	$Li_2CO_3 : CO_2$	7.00	7.00*
			$LiCl : AgCl$	6.96	6.96
			$Li_2CO_3 : Li_2SO_4$ (one experiment)	7.13	....
13.	Stas	1865	$LiCl : Ag$	7.006	7.003*
			Stas himself calculated	7.022	....
			$LiCl : LiNO_3$	6.92	6.96
14.	Dittmar	1889	$Li_2CO_3 : CO_2$	6.89	6.89

---

[1] This table is taken from Brauner's admirable chapter on this subject in Abegg's "Handbuch der anorg. Chemie," II, 1, 106. The references to the original papers are as follows: 1. *Schweigg. Journ.*, **22,** 93 (1817). 2. *Ann. chim. phys.*, **7,** 284 (1818). 3. *Gilb. Ann.*, **72,** 399 (1822). 4. *Schweigg. Journ.*, **54,** 231 (1827). 5. *Pogg. Ann.*, **15,** 480 (1829). 6. *Ibid.*, **17,** 379 (1829). 7. *Ibid.*, **48,** 361 (1839). 8. Sill, *Am. J. Sci.* [2], **22,** 349 (1856). 9. *Ann. chim. phys.* [3], **51,** 111 (1857). 10. Sill, *Am. J. Sci.* [2], **28,** 349 (1859). 11. *Lieb. Ann.*, **121,** 93 (1862). 12. *Compt. rend.*, **54,** 366 (1862). 13. Stas, *Oeuvres Completes*, **1,** 710 and 717. 14. *Proc. Roy. Soc. Edinburgh*, **35,** II, 429.

All excepting one of these determinations was made more than forty years ago, and the most recent, made twenty years ago, involved the use of a questionable method. Hence it is clear that a redetermination of the atomic weight would be desirable, even if it were not essential for the precise evaluation of silver and oxygen with the help of lithium perchlorate. Lithium alone among the five alkali metals has not received reasonable attention in this respect in recent years.

Of these twenty-three values found for the atomic weight of lithium, only those given in the last column of the table referred to the standard Ag = 107.88 are worthy of serious consideration. A few words discussing their merits and defects, in chronological sequence, will not be misplaced.

Mallet in 1856 purified his lithium chloride by dissolving it in alcohol and ether, but Stas has shown[1] that by this method the salt cannot be separated from the chlorides of the other alkaline metals. He fused and weighed it in a covered platinum crucible—a process which must have given an alkaline product, in spite of the fact that ammonium chloride was added. Moreover, the hygroscopic nature of the chloride prevents it from being exactly weighed without greater protection from laboratory moisture. In two experiments the silver chloride was weighed, and in one the solution was titrated against a known weight of silver, following the method of Pelouze. The latter method in its old form gives too low results. The various errors seem to have counterbalanced one another, for the average value, 6.94, is almost exactly correct. This happy result could hardly have been foreseen, however.

Diehl purified his lithium by repeated precipitation with ammonium carbonate, thirty precipitations being required to free it from sodium. The lithium carbonate was then dissolved in sulphuric acid and treated with barium hydroxide, the lithium hydroxide thus obtained being converted into carbonate. This was dried at 130° and decomposed in a Bunsen apparatus by means of dilute sulphuric acid, the carbon dioxide being determined by the loss in weight of the apparatus. Four experiments were performed, the average value obtained being 7.03, but no vacuum corrections were applied, nor was a counterpoise used in weighing. The possibilities of uncertainty are so great that no one to-day would be disposed to accept the result without question.

Troost purified lithium carbonate by repeatedly dissolving it in cold water saturated with carbon dioxide and reprecipitating it by boiling the solution. In two experiments it was dried at 100°, mixed with powdered, ignited quartz, and the carbon dioxide determined by the loss of weight on heating. In one experiment it was converted into the sulphate. In two experiments lithium chloride was dehydrated in dry hydrochloric acid gas, which was afterwards displaced by dry air. The chlorine was determined by weighing as silver chloride, and the mean value obtained for the atomic weight was 6.96. This outcome possesses the virtues and defects of Mallet's work.

---

[1] Stas, *Oeuvres Completes*, 1, 691.

Dittmar purified lithium carbonate by the method of Troost, but did not obtain a pure salt. He fused it in a current of dry carbon dioxide, the pressure varying from one to two atmospheres. By this means the formation of oxide was prevented. The carbonate was decomposed by dilute sulphuric acid, the gas evolved being absorbed by potassium hydroxide and weighed. The work was ingenious but very crude; the mean of ten results varying more than one-half per cent. was 6.89.

Stas's work was far more careful than any cited above, although the final result was really not as accurate. He purified his lithium salt according to the methods of Diehl and of Troost. After removing most of the other metals by dissolving the chloride in alcohol and ether, the lithium was precipitated with ammonium carbonate seven times before it was found to be free from sodium. The lithium in the mother liquors was precipitated as carbonate, and this was purified by conversion into soluble bicarbonate, and reprecipitation of the solution by boiling—a very troublesome operation requiring several days. Two such treatments gave a product free from sodium. Both methods are extremely wasteful, 1200 grams of fairly pure carbonate yielding only 145 grams of the purest salt. This was converted into chloride by heating in a platinum boat to 175° in a current of dry hydrochloric acid gas. The chloride was then maintained in a state of fusion for twenty minutes, and finally cooled in nitrogen, after which it was weighed in a vacuum. The solid salt was subsequently dropped into a solution containing the theoretical amount of silver dissolved in nitric acid, and the titration was carried on exactly as in the work on sodium chloride. The errors incident to this process have been pointed out by Richards and Wells.[1] Impurity in the silver and occlusion of silver nitrate by silver chloride tended to lower the atomic weight; impurity in the lithium chloride, and the error of method of determining the end point, tended to raise it. Stas himself calculated as the mean atomic weight of lithium from three experiments 7.022, but this becomes 7.003 if modern values for silver and chlorine are substituted.

He also determined the ratio $LiNO_3 : LiCl$ by dissolving the chloride in water in a large flask, evaporating with excess of nitric acid, and finally fusing the nitrate. Using modern values for nitrogen and chlorine, the atomic weight of lithium calculated from the mean of three experiments, is 6.961—a value much more nearly correct than the other.

Stas always found his lithium chloride alkaline to litmus, even when it had been heated in hydrochloric acid until half the salt had volatilized.

---

[1] This Journal, 27, 459 (1905).

It is difficult to account for this fact, yet it helps to explain the excessively high value for the atomic weight which he obtained. His lithium chloride volatilized in hydrochloric acid without leaving any residue, but this would not preclude the possibility that chlorides of the other alkali-metals were present. In some later work on lithium,[1] he failed to obtain, by the means previously employed, a sample of lithium carbonate which would not show the sodium line upon very careful spectroscopic examination. It was necessary to volatilize in the oxyhydrogen flame, one-third or one-half of the carbonate, in order to obtain a residue of oxide absolutely free from sodium. From this oxide, he was unable to prepare pure lithium chloride, and he remarked that he believed it impossible to obtain that salt absolutely free from sodium unless every trace of dust could be excluded. It is obvious that the purification of lithium salts demands further attention.

Up to the present time, the most accurate work on this element has been usually supposed to be that of Stas. Since the errors in his work on the chlorides of potassium, sodium, and lithium are similar, and his values for the first two metals are too high, we should naturally expect the same to be true of lithium. The error was quite noticeable in the case of potassium, still more pronounced with sodium, and, as will be shown, was greatest of all with lithium.

In reviewing the foregoing results, which vary so widely, it seemed clear that the reason for the incompatibility of the values obtained for lithium, was to be sought not only in the methods of analysis, but also in the impurity of materials. Accordingly the first step of the present research was a careful study of the various practicable methods of purifying salts of lithium. The next procedure was obviously the application to the purest lithium material of the methods already so thoroughly studied in this laboratory in the cases of sodium and potassium. Some of the details of these methods were improved, and these improvements will be described in due course.

Balance and Weighing.

The excellent and sensitive Troemner balance which has served in many similar researches was used in the present work. Successive weighings of the same object rarely differed more than 0.02 mg.

The Sartorius gold-plated brass weights and rider were standardized from time to time by the method usually used at Harvard.[2] All weighings were made by substitution, using a counterpoise similar to the object which was being weighed, so that the weights required were never large in amount, and the influence of changes in atmospheric conditions was negligible.

[1] *Oeuvres Complètes*, III, 324.

[2] Richards, THIS JOURNAL, 22, 144 (1900).

The vacuum corrections applied were as follows, the density of the weights being 8.3.

	Density.	Vac. cor. per gram.
Silver	10.49	—0.000030
Silver chloride	5.56	+0.0000732
Lithium chloride[1]	2.068	+0.000436
Lithium perchlorate	2.428	+0.000350

The Preparation of Materials.

All the solid, liquid and gaseous materials used in this research were purified with the greatest care. The most insidious sources of impurity in work of this kind are dust and the various gases sometimes contained in the air of the laboratory, and the most efficient methods of purification may fail to give a pure product unless careful attention is paid to this fact. The presence of dust, which always contains sodium, was especially noticeable in the preparation of pure lithium salts, where sodium was the element most difficult to remove. It was found that a lithium salt free from sodium, after being recrystallized in the usual way, always acquired traces of this element. The air of the room was, therefore, kept as pure as possible, and all evaporation, and handling of solutions and salts in the final work, were conducted in a large glass case. Vessels containing pure material were always kept covered and under bell jars when not in use. When it was necessary to work under the hood, a large, clean glass plate was suspended above the apparatus, to protect it from particles of dust falling from above. All heating was conducted electrically in order to avoid the deleterious effects of products of combustion.

Since most of the heating apparatus was constructed in this laboratory during the progress of the work, a brief description of it may not be inappropriate. The resistance material was "nichrome," an alloy of nickel, iron and chromium, which withstands fairly well a temperature of 1000°. It was generally used in the form of a ribbon, 1.5 to 3 millimeters wide. A small electrical stove or hot plate for conducting evaporations was made by winding this ribbon on a quartz plate, which was then covered with another thin plate of the same material, and the whole suitably mounted and insulated with asbestos. Another form, particularly adapted for heating flasks and dishes, was made by winding layers of wet sheet asbestos and the ribbon concentrically till the desired size was obtained; the roll, while still moist, was then pressed against the vessel to be heated and shaped to fit it. When dry, the mass of asbestos with its embedded ribbon, retained its form, and was mounted on asbestos board. A drying oven was made by winding a three-liter beaker with the ribbon, and jacketing it with heavy asbestos. By cutting through this jacket at one place, a window was formed, through which the interior could be observed.

---

[1] Baxter, *Am. Chem. J.*, 31, 558 (1904).

A temperature of 400° was easily obtained. A porcelain tube for fusing silver was wound with the ribbon and then covered with thick asbestos. When it was desired to heat a glass tube, and at the same time observe the interior, the ribbon was left bare, and the convolutions were far enough apart so as not appreciably to obstruct the view. The value of electrical heating, both as to cleanliness and wide range of application, was emphasized in the present research.

The vessels used in purifying materials were usually of quartz or platinum. Where glass was unavoidable, the best Jena glass was employed.

Water.—Distilled water of the laboratory was twice redistilled, once from alkaline permanganate and once alone, using pure tin condensers, without rubber or cork connections.[1] In special cases the water was condensed and collected wholly in platinum. Dust was carefully excluded by passing the end of the condenser through a hole blown in the bulb of a small flask, which rested on the mouth of the large Jena flask in which the water was collected and stored. Water was always distilled just before use.

Nitric Acid.—Carefully tested pure nitric acid of commerce was redistilled, using a platinum condenser. When required to be free from chlorine the first portion was rejected and the acid redistilled until it showed no trace of this element when examined in the nephelometer.

Hydrochloric Acid.—The pure acid of commerce was boiled with a little pure potassium permanganate, and then repeatedly distilled, using a quartz condenser.

Ammonium Fluoride.—Baker's best hydrofluoric acid, which was already very pure, was distilled once in a platinum retort, and neutralized by distilling into it, through a platinum tube, pure ammonia from a concentrated solution of the gas.

Ammonium Carbonate.—The purest commercial salt was dissolved in water containing ammonia, and distilled in a platinum retort. Any trace of impurities contained in the product must have been volatile ones, which could exercise no harmful effect in the present case.

Hydrazine Hydrate.—This substance was prepared by distilling to dryness in platinum a mixture of hydrazine sulphate and potassium hydroxide in solution, using double the theoretical quantity of the latter substance. The resulting solution was distilled again from the small residue of alkali which had been carried over into it; the dilute portion coming over first was distilled yet once more in order to concentrate it, the first fractions, containing almost nothing but water being rejected. The substance was collected and preserved wholly in platinum, as were also the ammonia and ammonium fluoride.

Perchloric Acid.—This was prepared by a modification of the method of Kreider.[1] Since sodium perchlorate can now be obtained in large quantities, the preparation of the stable hydrated acid is a comparatively simple operation, quite free from the dangers and difficulties involved in preparing the unstable anhydrous compound.

---

[1] Richards, *Proc. Amer. Acad*, 30, 380 (1894); *Chem.-Ztg.*. 1907, No. 73, p. 899.

A saturated solution of sodium perchlorate was poured into two and one-half times its volume of pure concentrated hydrochloric acid (density, 1.20). After thorough agitation the sodium chloride was allowed to settle, the clear liquid was siphoned off, and the sodium chloride drained in a funnel by suction, and washed with a little more acid. The solution, containing hydrochloric and perchloric acids, with a little salt of sodium, was evaporated until dense white fumes of perchloric acid began to appear. The liquid was then found to be entirely free from hydrochloric acid. At this point the concentration of the perchloric acid is approximately that of the dihydrate—about 70 per cent. If distilled under ordinary pressure, where it boils at 203°, there is considerable decomposition, involving a loss of perhaps 10 per cent. The crude acid was therefore usually distilled under 150 to 200 mm. pressure, with almost no decomposition, but for the final distillation a pressure of 15 to 20 mm. was not exceeded. At first the acid was condensed in a platinum condenser bent at right angles and having its upper end slightly conical to fit into the constricted neck of a two-liter flask of resistant glass. The constriction was carefully ground until the platinum fitted it tightly. It was found that this joint held a vacuum very effectively after the flask and condenser had been pressed firmly together. The other end of the condenser passed through a rubber stopper fitted into a hole in a bell jar containing the platinum dish to receive the distillate. While the excess of water was being distilled off, the acid bumped rather badly; but when the concentration of the acid became that of the constant boiling mixture, this distilled rapidly and smoothly without any sign of ebullition. The yield is practically the theoretical.

Even when distilled under a pressure of 15 mm. the acid had a faint odor, resembling that of the oxides of chlorine. It seemed possible, therefore, that the hot liquid might attack slightly the platinum condenser, although no evidence of such an effect was observed. Accordingly, in preparing the purest acid, we decided to condense and collect it in quartz vessels. To the quartz condenser was attached the half-liter distilling flask, into the neck of which was fused a dropping funnel, terminating in a capillary at the bottom of the flask. In this way acid could be introduced continuously during the distillation. The connection between the flask and the quartz condenser gave much trouble. At first a carefully ground joint was used, the quartz forming the inner portion, but it was found that since the coefficient of expansion of glass is far greater than that of quartz, such a joint will invariably crack, even when exposed to a change of temperature of only 75°. If the outer portion is glass, it cracks on cooling; if quartz, on heating. The only possible joint between these two materials which will allow expansion and contraction, is one having two flat faces ground together as in Fig. 1.

---

[1] *Z. anorg. Chem.*, **9**, 343 (1895); *Am. J. Sci.* [3], **49**, 443. Kreider and Breckenbridge, *Z. anorg. Chem.*, **13**, 161 (1896); *Am. J. Sci.* [4], **2**, 263.

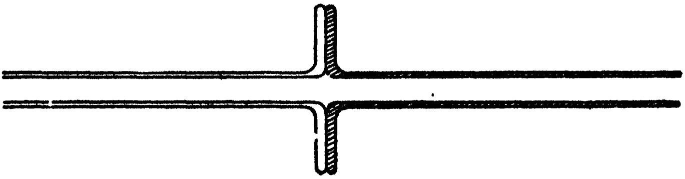


Fig. 1.

Such a joint is easily made by forming a collar on the end of each tube, grinding them until perfectly plane, and finally polishing with oil and rouge. The two faces are held tightly together by a rubber band or a spring. Such a joint, without any lubricant, held a vacuum very effectively, and was entirely unaffected by changes of temperature. The joint was so placed that any condensed liquid coming into contact with the glass part would run back into the distilling flask.

After at least three previous distillations, the acid was finally distilled through the quartz condenser directly into a quartz flask, and all possibility of introducing impurity in this process was avoided.

The question of the purity of the acid thus obtained was carefully investigated. All the possible impurities must be those present in the sodium perchlorate and hydrochloric acid, and the only acids likely to remain after concentrating the crude acid, are sulphuric and phosphoric; the others are either destroyed or volatilized.

In order to determine how readily sulphuric acid could be separated from perchloric, a mixture of the latter with two per cent. of sulphuric acid was fractionated. After three distillations in which only 10 per cent. was rejected, 90 per cent. of the last distillate proved to be entirely free from sulphuric acid and 9 per cent. more contained so little that the residue left after evaporating off all but 1 cc., showed a barely visible opalescence upon the addition of barium chloride. Phosphoric acid is even easier to remove. The residue remaining after the distillation of the crude acid from 8000 grams of sodium perchlorate, consisting mainly of sodium salts, contained a little sulphate and a trace of phosphate, but the last 20 cc. of acid distilled from this showed no trace of phosphoric acid.

Since the acid was never distilled less than four times, each time rejecting a small residue, its purity was evidently quite beyond reproach. If further proof was needed, this was furnished by the fact that the residue of 5 cc., remaining after distilling off about 8500 grams of acid (previously twice distilled) and which must have contained practically all the sulphuric acid present in the entire amount, showed only the merest trace of it, not over 0.0001 gram.

Silver.—The preparation of pure silver has been fully described by Richards and Wells[1] and the details need not be repeated here. Four samples were prepared.

Sample A. Pure silver nitrate was recrystallized five times from dilute nitric acid, using vessels of Jena glass. The crystals were centrifugally drained in platinum funnels. The silver was then precipitated by ammonium formate, prepared from redistilled ammonia and formic acid, and after thorough washing, it was fused on pure lime in a current of dry hydrogen, generated by the action of "hydrone"[2] on water. The boat was provided with partitions, so that buttons of a suitable size were formed. These were etched with dilute nitric acid, washed, and dried in a vacuum at 400°.

Sample B was prepared in a similar way except that it was recrystallized twice in glass and four times in platinum, and the reduction with formate was conducted in a platinum dish.

Sample C was obtained by precipitating the mother liquors from A twice successively with formate, and then fusing on pure lime with a blast lamp.

Sample D was prepared from pure silver nitrate which had been once recrystallized, precipitated with formate, and fused on lime in hydrogen. This and sample C were used only as the source of silver nitrate in the precipitation of silver chloride to be weighed.

Experiments were made to determine whether the platinum dish was attacked by the hot nitric acid used to dissolve the silver nitrate, the dish being weighed before and after the operation. There was no loss in weight when the contents of the dish were stirred with a smooth glass rod, but when a platinum spatula was used, and the stirring was very vigorous, a loss of 0.24 mg. was observed, doubtless due to abrasion by its rather sharp edges. The precipitation of silver by formate caused no change in the weight of the dish.

Lithium Chloride.—The most common impurities in lithium salts and likewise the most difficult to eliminate are those elements most nearly related to it—the metals of the alkalies and alkaline earths. In the material which formed the source of the lithium chloride used in this work, the only impurities present in appreciable amounts were iron, calcium, potassium, sodium and probably magnesium. It is true that none of the latter was ever found, but this is probably due more to the difficulty of detecting small traces of it in the presence of large quantities of lithium, than to its entire absence. In Kahlbaum's lithium chloride, which formed part of the original material, no calcium, potassium or magnesium could be found. Since the iron was very easily removed, the impurities whose separation demanded careful investigation were potassium, sodium, calcium and magnesium. The relative effects of these on the atomic weight of lithium vary in the order given, that of potassium being the greatest.

---

[1] This Journal, 27, 472 (1905).

[2] This is the trade name for an alloy of sodium and lead.

Attention was first turned to the methods of eliminating potassium and sodium, which go together. Those employed by previous investigators were either inadequate or extremely wasteful. To the first class belongs that of dissolving the chloride or nitrate in a mixture of alcohol and ether. This was found to be effective in removing the greater part of the sodium from a crude chloride, especially if the solution were treated with hydrochloric acid gas until part of the lithium chloride was precipitated; but aside from this, it has no value. Precipitation by means of ammonium carbonate is effective, but the yield is very small, since only half of the lithium can be precipitated in one operation, owing to the solvent action of the ammonium salts. The conversion of the normal carbonate into bicarbonate demands too great a volume of solution, and is entirely too tedious where large quantities are required.

The most common method of purification—the recrystallization of soluble salts—seems to have received no attention, and accordingly various salts were tested with regard to their fitness for this purpose. With lithium chloride, the amount of sodium steadily decreased upon successive recrystallization until only a trace remained, but this trace was very hard to remove. Moreover, the solubility of the salt is so great that the process is very wasteful. The oxalate was almost useless in this respect. Recrystallization of the formate was fairly effective, but its electrolytic oxidation to carbonate was more so. Both the perchlorate and nitrate gave good yields, and the elimination of sodium was rapid, especially in the case of the nitrate. Care must be taken, however, to crystallize this latter salt below 29.6°, the transition point between the hydrated salts $LiNO_3.\frac{1}{2}H_2O$ and $LiNO_3.3H_2O$. Above 61° the anhydrous salt crystallizes, and under these conditions the separation from sodium is poor. The perchlorate crystallizes as $LiClO_4.3H_2O$.

These two salts were, therefore, selected as giving the most favorable results, but even with their help it is almost impossible to eliminate the last traces of sodium. It was evident that some method involving precipitation would be necessary. A search among the insoluble salts of lithium showed that the solubility of the fluoride is only 2.7 grams per liter—one-fifth that of the carbonate—and that this solubility is not appreciably affected by the presence of ammonium salts. Sodium fluoride is sixteen times, and potassium fluoride three hundred and forty times more soluble. Evidently the precipitation of lithium fluoride by ammonium fluoride ought therefore to be an extremely efficient means of removing sodium, without appreciable loss of lithium, and this was found to be true. Solutions of ammonium fluoride and of a lithium salt were run slowly into boiling water in a platinum dish, with constant stirring, taking care to avoid any great excess of either. The lithium fluoride formed under these conditions was coarsely crystalline and the precipitation was practically complete. The precipitate was transferred to platinum funnels and washed several times with water, using centrifugal drainage. Such washing has been shown to be very effective.[1] If the original material contained comparatively little sodium, this precipitate was found to be entirely free from it, upon careful spectroscopic examination, and a repetition of the precipitation was sufficient to attain this end, even with very crude material. The pure fluoride was then converted into either nitrate or perchlorate by heating in a platinum retort with the corresponding acid—the distillate when perchloric acid was used being pure hydrofluoric acid, which was used again. When nitric acid was used, three or four times the theoretical quantity was required, owing to the slight difference in the boiling points of the acids. Thus it was possible to obtain, rapidly and without appreciable loss, lithium nitrate or perchlorate absolutely free from sodium. Some difficulty was experienced when making the spectroscopic tests, in obtaining a flame free from sodium, but if the air of the room was not dusty, this could be accomplished by using a small blast flame, supplied with pure washed air.

This method does not, however, eliminate calcium and magnesium, since the fluorides of both these metals are less soluble than that of lithium. Previous treatment of the solution with lithium fluoride is not very effective, but the addition of ammonium oxalate removes nearly all the calcium. The addition of lithium carbonate is yet better, only traces of calcium and magnesium remaining. These may be wholly separated by the recrystallization of the nitrate or the perchlorate. From a sample of lithium nitrate to which had been added 10 per cent. each of lithium sulphate, and calcium and magnesium as nitrates, there was obtained after four recrystallizations a salt which gave no tests for any of these impurities. The recrystallization of the perchlorate was almost equally effective.

The method of purification finally adopted was, therefore, essentially the following: The fluoride, free from sodium but containing possible traces of calcium, magnesium, and sulphate, was converted into nitrate or perchlorate as described. These salts, free from fluorine, were recrystallized several times, using centrifugal drainage. The efficiency of this method may be shown by the fact that 70 grams of free acid were so completely removed from 400 grams of lithium perchlorate by three recrystallizations that less than a milligram of free acid remained. Since even in the mother liquors from the first recrystallization no calcium, magnesium, or sulphate could be detected by the ordinary tests, there is no doubt that this recrystallized nitrate or perchlorate was exceedingly pure. All silica must have been removed when the fluoride was dissolved in acid. The final step of this sequence of operations alone remained to be taken, namely, the conversion of the salts into chloride.

---

[1] Richards, This Journal, 27, 104 (1905).

In the case of the nitrate the conversion into chloride was not difficult. The solution was poured into a hot, concentrated solution of ammonium carbonate, which had been distilled in a platinum retort, and the precipitated lithium carbonate was washed several times with hot water, using centrifugal drainage. It is essential that hot and concentrated solutions be used; otherwise, the yield of carbonate—at best only 50 per cent.—will be much smaller. The precipitate is coarsely crystalline and easily washed. This process also serves as a means of further purification. The carbonate was dried at 300°, dissolved in slightly less than the theoretical amount of the purest hydrochloric acid which had been twice distilled and condensed and collected in quartz, and subsequently filtered from excess of carbonate. The solution contained a little nitrate, and to convert this into chloride without fear of attacking the platinum, a solution of pure hydrazine hydrate, distilled in platinum, was added, and then excess of hydrochloric acid. After boiling the solution a few minutes, all the nitrate was reduced, and there remained a solution of pure lithium chloride with a little hydrochloric acid and hydrazine chloride, both of which were completely volatilized in subsequent operations. The chloride was recrystallized once or twice, and dried, and it was then ready for analysis. During the purification it was treated only with materials prepared in quartz or platinum.

The conversion of lithium perchlorate into chloride was not so simple. At first the solution was mixed with ammonium chloride and the crystals of ammonium perchlorate were separated by filtration. The solution containing the lithium chloride was evaporated and ignited, but unfortunately, on ignition the small amount of perchlorate remaining caused the evolution of considerable chlorine, which attacked the platinum badly. If quartz was used, it also was attacked, the salt becoming alkaline. Careful ignition in platinum was the method finally adopted, the presence of the metal being decidedly the lesser evil; but it was necessary to regulate the temperature very carefully, otherwise the action became too violent. The chief action on the platinum occurs only towards the end of the operation, when a higher temperature was required. It was found advantageous to halt the operation at the point where the mass became pasty, to dissolve the product in water and evaporate to dryness, thus uniformly diluting the perchlorate with an excess of chloride. Sometimes chloride from a previous operation was added. If the final heating was performed in air, the platinum was always slightly attacked, but if this were done in an atmosphere of hydrogen, the slightly alkaline chloride could be fused without any appreciable effect on the vessel. The chloride thus prepared was freed from platinum and crystallized two or three times and was then ready for analysis. This method of preparation must have given a product absolutely free from traces of other halogens. In all the preparation work, exclusion of dust was the greatest difficulty. It was found desirable to shorten all the processes whenever this could be done, so as to expose the material as little as possible. The principal impurity introduced by dust is sodium. It seemed best, therefore, to effect the elimination of the last traces of sodium towards the end of the purification, rather than at the beginning.

Several samples of lithium chloride were prepared by these methods, platinum vessels being used throughout. The material which served for the preparation of sample A consisted of chloride prepared from commercial carbonate and freed from most of its sodium by treatment with alcohol and ether. It was recrystallized six times, precipitated as fluoride and added to another specimen of fluoride which had been precipitated from the mother liquors, twice recrystallized as perchlorate, and finally precipitated yet again as fluoride. Subsequently, it was all converted into perchlorate, twice recrystallized, treated with ammonium chloride to remove most of the perchlorate, and ignited in platinum. The platinum which was dissolved was removed by a solution of hydrazine, and the chloride was crystallized once more from hydrochloric acid solution. Owing to an accident in which most of it was lost, this sample was sufficient for only one analysis. It contained a barely visible trace of sodium.

Sample B was prepared from commercial lithium chloride, also purified by solution in alcohol and ether. The main portion was twice precipitated as fluoride. To this precipitate was added some fluoride precipitated from the last mother liquors of A, and the whole was converted into perchlorate, which was recrystallized three times. It was then treated with ammonium chloride, and finally fused in platinum. The platinum which was dissolved was removed as usual by precipitation with hydrazine, and the salt was evaporated to dryness. It also contained a trace of sodium.

Sample D. To the mother liquors from the last three recrystallizations of sample B were added some fairly pure residues of lithium chloride, and the whole was precipitated as fluoride. At this point it was free from sodium. After conversion into perchlorate it was recrystallized six times, ignited to chloride in platinum, fused in hydrogen, and twice recrystallized as chloride. This was D_3. The mother liquors from these two recrystallizations formed D_4. The mother liquors from the last three recrystallizations of the perchlorate were once recrystallized; the perchlorate was ignited to chloride and crystallized once. This was D_2. The mother liquor formed D_1. All these preparations contained a trace of sodium, in spite of the fact that previously the material had been free from this element, and no glass vessels had been used. The sodium undoubtedly came from traces of dust.

Sample C. Residues of lithium nitrate and bromide from other work on lithium were treated with ammonium oxalate to remove calcium, and twice precipitated as fluoride. The remainder of sample B was likewise precipitated as fluoride and added to this. All of it was free from sodium. It was converted into nitrate by evaporation in a platinum retort with the purest nitric acid and water, freshly distilled. After expelling all the acid, it was dissolved in water and filtered from a slight residue containing fluoride, and platinum. The solution contained no platinum, and was absolutely free from sodium. The nitrate was recrystallized three times, poured into freshly distilled ammonium carbonate, and the precipitate washed and dried. It was almost completely dissolved in the purest hydrochloric acid, filtered, more acid added, and then a little hydrazine hydrate. Boiling soon destroyed the nitrate present, and the pure chloride was crystallized once. At last, this sample was entirely free from sodium, and therefore was worthy to form the basis of some of our best experiments.

Sample E was prepared in much the same way as C. Two kilograms of Kahlbaum's best lithium chloride, nearly anhydrous, were available as raw material. Tested carefully, it showed no potassium, calcium or magnesium, and only small traces of iron, but as usual it contained considerable sodium. The salt was dissolved in about 8 liters of pure water, and agitated with pure lithium carbonate, being allowed to stand over night in large Jena flasks. The precipitate contained iron but no calcium. The perfectly clear, colorless solution after filtration was evaporated in a platinum dish, and crystallized with centrifugal draining, and the mother liquor was evaporated further, the second group of similarly drained crystals being added to the others. The whole was recrystallized, and treated again in the same way. In order to eliminate the small amount of sodium which still remained, the lithium was precipitated as fluoride. The coarse-grained, easily washed precipitate was collected upon a Büchner funnel, and was washed two or three times, being each time stirred up with the water. The washed material was whirled in the platinum centrifuge, and then washed six times, taking four milliliters of water each time, and draining completely with centrifugal action after each washing. The last wash water contained only a faint trace of chloride and the salt was found to be almost wholly free from sodium when examined in the spectroscope. In this way were obtained 620 grams of dry, very pure lithium fluoride, which served as a basis for yet further operations These successfully removed the traces of impurity still remaining, as the following description shows.

The coarse-grained powder was now decomposed by heating with a large excess of nitric acid in successive additions. About six times the theoretical quantity of 70 per cent. nitric acid was required in all, diluted with an equal bulk of water, it having been found that the diluted acid was more efficient than the concentrated acid. After the expulsion of the nitric acid, the nitrate was slightly alkaline, and no trace of platinum was found by the potassium iodide test in the filtrate, although the residual precipitate of lithium fluoride contained platinum. In order to be sure that no platinum was present, the clear filtrate was treated with a little hydrazine hydrate, but no change occurred All the nitrate was finally evaporated with excess of nitric acid until neutralized, and the nitrate was crystallized three times with centrifugal drainage in platinum. The trace of sodium present in the fluoride had now entirely been eliminated. The mother liquors from the last two crystallizations were evaporated and twice recrystallized again, yielding material free from sodium, like the other crystals to which they were added.

The lithium was now precipitated as carbonate—a process which rendered certain the elimination of any traces of fluoride which may have found its way through the successive recrystallizations of the nitrate.

The ammonium carbonate for this purpose was prepared by distilling the substance with water in a platinum still into a platinum dish. The solution was heated to the point of obvious decomposition and the lithium nitrate was then poured into it, the whole being digested for a time at a high temperature. The lithium carbonate was collected in platinum funnels, washed three times with hot water, using centrifugal drainage, and was dried at over 400° in an electric oven. Only about 250 grams of carbonate were thus obtained, a yield of less than 30 per cent. of the original fluoride.

The lithium carbonate was then dissolved in hydrochloric acid which had been twice distilled in quartz, rejecting the first and last portion each time. The solution was alkaline, because not quite enough acid had been added to correspond to the carbonate. The filtered solution was treated with a small amount of hydrazine hydrate and a considerable excess of hydrochloric acid. After evaporation, the solution which had originally given a strong test for nitrate with diphenylamine was found to be wholly free from this contamination. The purest water was now added, enough to make a hot saturated solution, and the substance was crystallized by cooling the platinum vessel in ice. The crystals were drained centrifugally in platinum and another crop was obtained from the mother liquor, and the combined material was redissolved and again recrystallized in the same way. In the least pure of the mother liquors an exceedingly faint trace of sodium was found, but the crystals after centrifugal drainage were entirely free from it as far as the most careful spectroscopic testing could show.

Most of the water was driven off from these crystals over the electric hot plate, and the stirred mass was heated in the electric oven at a high temperature until nearly all the ammonium chloride present had been volatilized. The mass weighed about 170 grams when dry, or about 17 per cent. of the lithium originally present as fluoride. A portion of this substance was broken into pieces in a clean warm agate mortar and used in Analyses 21-22, 30, and 31.

In spite of the fact that various methods had been used in these purifications, and the fact that some of them contained minute traces of common salt, the five preparations were all essentially identical, except from the point of view of the most critical experimenter. The maximum variation affected only the third decimal place in the atomic weight; the second figure was never in doubt. The two purest samples, which were wholly free from sodium, namely samples C and E, gave exactly the same result, within the limit of error of the experiments. This fact will become manifest when the detailed figures are presented, on pages 31 and 33.

The Drying and Weighing of the Lithium Chloride.

The final preparation of the salt for analysis consisted in expelling the last traces of water by fusion in a platinum boat in a current of dry hydrochloric acid gas and nitrogen, the operation being conducted in the apparatus usually used for this purpose at Harvard.[1] To avoid absorption of acid by the chloride, this gas was swept out by a current of pure nitrogen, before the salt solidified, and after cooling, the nitrogen was replaced by dry air. The boat was then transferred to the weighing bottle without contact with a trace of moisture, and weighed.

In the preliminary experiments the old form of "bottling apparatus"[1] was used for this purpose, but in the final series, the new form shown in Fig. 2 was employed.

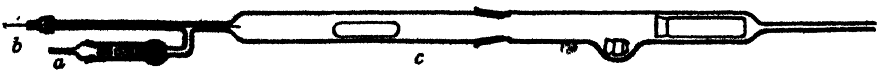


Fig. 2.

In this any possibility that moisture might gain access to the salt is excluded; the calcium chloride tube (*a*) is not removed and the glass rod used to push the boat into the bottle is passed through a short piece of rubber tubing at (*b*). When this apparatus was constructed of glass, evidence was found of the introduction of other alkali-metals into the lithium salt by the action of hydrochloric acid on the red hot tube. Hence in the final experiments, this portion of the apparatus (*a* to *c*) was made entirely of transparent quartz, and carefully ground into the other. The tube was heated by winding it with "nichrome" ribbon, through which a suitable current was passed, an arrangement that not only gave evenly distributed heat, but also allowed the progress of the fusion to be clearly observed. The apparatus was so constructed that by turning the proper stopcocks, either hydrochloric acid, nitrogen, air, or any desired mixture, could be passed through it. These stopcocks were so carefully polished with rouge that a trace of lubricant composed of a mixture of paraffin and pure rubber made them perfectly gas-tight.

---

[1] Richards and Parker, *Proc. Amer. Acad.*, 32, 59 (1896).

The nitrogen was prepared by passing air charged with ammonia over red-hot copper. Carbon dioxide was removed by means of potassium hydroxide solution, and the excess of ammonia, by passing the gas through a series of towers filled with glass beads moistened with sulphuric acid, the first two containing dilute, and the last three, concentrated acid. The last traces of water were removed by means of resublimed phosphorus pentoxide. Nitrogen prepared in this way usually contains a trace of hydrogen, which in this case was a distinct advantage, since it would counteract the effect on the platinum boat of any trace of oxygen that might be present.

The hydrochloric acid gas was prepared by dropping concentrated sulphuric acid into a solution of pure concentrated hydrochloric acid. It was dried by passing through three towers filled with pearls moistened with freshly boiled concentrated sulphuric acid, for it has been shown[1] that phosphorus pentoxide is unsuitable for this purpose. No sulphuric acid could be detected in the solution obtained by passing into water a large quantity of the gas thus prepared.[2]

The air, which was furnished by a water pump, was purified by passing successively through towers containing potassium hydroxide, silver nitrate and concentrated sulphuric acid, and was finally dried by phosphorus pentoxide. The entire apparatus was of glass, the different parts being fused together, when possible, or else connected by carefully ground joints.

In detail the procedure was as follows: Dry lithium chloride contained in the platinum boat, was placed in the quartz tube and a mixture of nitrogen and hydrochloric acid passed through it for an hour or two, in order to sweep out all the oxygen. The gases issued under slight pressure, the end of the exit tube dipping just below the surface of mercury, covered with water to absorb the acid. The temperature was very slowly raised so as to expel from the salt as much water as possible before fusion. The chloride was maintained in a state of fusion at a red heat from fifteen to thirty minutes, the longer time apparently causing no further change. During this time the surrounding gas consisted principally of dry hydrochloric acid. Bubbles always formed on the bottom of the boat and were removed only by carefully shaking the tube. The hydrochloric acid was then replaced by pure nitrogen, to remove any excess of acid dissolved in the fused salt, and when the issuing gas was neutral, the chloride was allowed to cool. It was quite transparent and colorless. Because fused sodium chloride was found to be essentially free from dissolved nitrogen,[1] it is reasonable to assume that the similar lithium salt contained no weighable quantity. After the nitrogen had been replaced by dry air, the boat was bottled and placed in a desiccator. No great difficulty was experienced in obtaining weighings agreeing within 0.02 mg., using a similar bottle as counterpoise. Of course the bottle containing the empty boat was always filled with dry air before being weighed. The platinum boat was always weighed separately before and after the fusion, and the loss in weight, if the operation had been carefully conducted, was only a few hundredths of a milligram—sometimes none at all. This correction, if added to the weight of silver chloride, had no appreciable effect on the results.

---

[1] Baxter and Hines, THIS JOURNAL, 28, 779 (1906).

[2] See also Baxter and Hines, *Loc. cit.*, p. 780.

The boat was placed in a three-liter Erlenmeyer flask of Jena glass, with a carefully ground and polished stopper, and about 0.05 or 0.08 liter of water was added. When the chloride was dissolved, the solution was perfectly clear, and it was usually tested for alkalinity by adding a very dilute solution of phenolphthalein, which had been colored very faintly pink by a trace of sodium hydroxide. It is not sufficient to add a colorless solution of the indicator, for the ever-present trace of carbon dioxide decreases the delicacy of the test. The color never became deeper, and on thorough shaking was discharged by the carbon dioxide. Methyl orange showed a perfectly neutral tint. There can be no doubt, therefore, concerning the neutrality of the salt within the narrow limits thus established. About one liter of freshly distilled water was then added to the flask; the boat was lifted out by means of a heavy platinum wire, bent at one end, and was washed seven times in a beaker, the washings being completely transferred to the flask. This method seemed preferable to dissolving the salt in a beaker and transferring it to the flask, for not more than a few milligrams of lithium chloride could have remained on the boat when it was lifted out, and this small quantity could be transferred without any risk of loss.

---

[1] Richards and Wells, THIS JOURNAL, 27, 513 (1905).

The lithium chloride was then ready for analysis. Both of the familiar methods for finding the amount of chlorine were used, namely, the weighing of the precipitated silver chloride on the one hand, and the determination of the necessary amount of silver on the other. These are discussed below in order.

The Precipitation and Weighing of Silver Chloride.

The precipitation of the silver chloride and all subsequent operations were carried out under red light in the dark room. To the solution of lithium chloride was added exactly the calculated amount of silver dissolved in a moderate excess of nitric acid, the concentrations of the solutions being about decinormal. The mixture was shaken vigorously for ten minutes and allowed to stand over night. The next day it was again shaken, and to it was added the excess of silver nitrate required for complete precipitation—about 0.05 or 0.06 gram of silver per liter. This method diminishes greatly the danger of occlusion of silver nitrate, as Richards and Staehler have shown.[1] The solution was shaken from time to time during the next day, and after standing until the supernatant liquid was perfectly clear, it was ready for filtration.

In a few of the preliminary experiments, the Gooch perforated platinum crucible with asbestos mat was used, with all the precautions previously adopted in this laboratory. In all others a Gooch-Munroe crucible[2] was used. The complete removal of silver chloride from the platinum sponge, when preparing for a new analysis, required treatment with concentrated ammonia for at least twelve hours, followed by a very thorough washing. The crucible was always dried over night at 250°, and a perforated platinum plate was placed upon the sponge to prevent rupture by the contraction of the silver chloride as it dried. This crucible was of the special shape recently described by one of us.[3]

The clear solution was poured through the crucible, and the precipitate was washed four times by decantation with a cold acid solution of silver nitrate, about two-hundredths normal, the precipitate being thoroughly agitated by rotary shaking each time. The filtrate and washings were united and were always practically free from excess of chlorine, so that a constant correction of 0.04 mg. of silver chloride per liter was applied to them.[4] The precipitate was then washed ten times with very dilute nitric acid, cooled in ice to reduce the solubility of silver chloride, and finally transferred to the crucible by means of a jet of pure, cold water from a hydrostatic wash-bottle. The entire process was conducted under a clean pane of glass to prevent dust from falling into the crucible. The latter was finally wiped with a clean cloth and heated in an electric oven, gradually increasing the temperature to 250°, where it was maintained at least ten hours. After it had been weighed, the main mass of silver chloride was separated from the platinum disk and fused in a covered quartz crucible contained in a larger one of porcelain. Since the cover was transparent, it was possible to free the fused chloride from the bubbles which invariably adhered to the crucible, without danger of loss from spattering, by carefully rotating the crucible. With one or two exceptions, the fused silver chloride was perfectly colorless and transparent, showing the absence of organic dust and occluded silver nitrate. The loss on fusion was very small, never more than a few hundredths of a milligram per gram. The correction for the entire weight of silver chloride was calculated as usual from that of the portion fused, always over 90 per cent. of the total.

---

[1] THIS JOURNAL, 29, 632 (1907). Richards and Staehler, *Publ. Carnegie Inst., Washington*, 69, 15.

[2] Snelling, *Ibid.*, 31, 456 (1909).

[3] Richards, THIS JOURNAL, 31, 1146.

[4] Richards and Wells, THIS JOURNAL, 27, 487, 517 (1905). See also Baxter, THIS JOURNAL, 28, 1322 (1906).

The flask was carefully rinsed out with ammonia, to remove any chloride that might have escaped observation. This with the washings, was tested as follows: To the total washings, exclusive of those with dilute silver nitrate, was added 0.07 gram of silver as nitrate, and after the opalescence had appeared, it was dissolved by pouring in the ammoniacal rinsings. The volume was then made up to one liter. A standard solution was prepared, containing in one liter a known amount of chloride, and the same quantity of ammonia and of silver present in the washings. Twenty-five cc. of each solution were pipetted into a nephelometer[1] tube, 2 cc. of dilute nitric acid added to each and the contents stirred with a carefully cleaned glass stirrer. The tubes were covered with glass caps having a plane top, and allowed to stand from three to five hours, until constancy was attained. If the tubes were not nearly alike, a new standard was prepared. Several comparisons were always made and found to agree within reasonable limits of error only when extreme care was used in preparing the solutions and in excluding dust. By the use of ice-cold wash water, the total nephelometer correction was reduced from over 1 mg. to about 0.35 mg., often less, owing to the decrease in solubility of silver chloride. This matter will subsequently be discussed in detail.

The following table gives the results obtained in the preliminary experiments.

The first two analyses have little value since the technique of the process had not then been mastered and the material was purified only by six recrystallizations as chloride, and was known to contain impurities. No. 10 was rejected because it was found that all the silver chloride from the previous analysis had not been dissolved out of the Munroe crucible.

---

[1] Richards and Wells, *Am. Chem. J.*, 31, 235 (1904).

RATIO OF LITHIUM CHLORIDE TO SILVER CHLORIDE.

Preliminary Series.

No. of analysis.	Preparation of LiCl.	Weight of fused LiCl, vacuum.	Weight of fused AgCl, vacuum.	$\frac{LiCl}{AgCl}$.	Atomic weight of Li. Ag = 107.88.
1	O	4.01994	13.59125	0.295774	6.938
2	O	6.32840	21.39635	0.295770	6.939
3	A	8.99620	30.41341	0.295797	6.942
4	B	4.66824	15.78111	0.295812	6.944
5	B	5.43032	18.35734	0.295812	6.944
6	B	5.10725	17.26504	0.295815	6.944
8	D_1	5.74000	19.40375	0.295819	6.945
9	D_2	5.42038	18.32417	0.295805	6.943
11	D_3	5.21573	17.63280	0.295797	6.942
12	D_4	6.56925	22.20716	0.295817	6.945
13	D_8	4.84268	16.37121	0.295805	6.943
					6.943

In none of these analyses was the material wholly above reproach, for it all contained traces of sodium. Part of this impurity was present in the original salt, and those specimens (A and D_3) which show less sodium in the spectroscope gave a lower value for the atomic weight. Part of the sodium, however, may perhaps have come from the glass tube used to contain the boat in which the lithium chloride was fused. This conclusion was drawn from the fact that material thus fused showed in the spectroscope more sodium than it had possessed before. Nevertheless, these preliminary results are far nearer the truth than the work of any other experimenter.

In order to avoid the vitiating circumstances every conceivable precaution was taken in the final series recorded below. Both the samples of lithium chloride used were proved to be free from any visible trace of sodium discernible upon careful spectroscopic examination. This means, of course, a very high degree of purity. Moreover, the platinum boat during the fusion of the salt was contained in a tube of pure quartz. In this way only can a pure dry sample of lithium chloride be obtained, which will show no trace of sodium in the spectroscope.

As a result of these precautions the values of the atomic weight obtained were appreciably lower than those of the preliminary series, and they agreed distinctly better among themselves. The following table explains itself.

Analyses 19 and 20 were omitted because of accidents which rendered them valueless. Experiments 14 to 17 inclusive had previously been used for determining the weight of silver needed for the exact precipitation. This part of these experiments is recorded in the table on page 33, under the numbers 26 to 29.

RATIO OF LITHIUM CHLORIDE TO SILVER CHLORIDE.

Final Series.

No of analysis.	Preparation of LiCl.	Weight of fused LiCl, vacuum.	Weight of fused AgCl, vacuum.	$\frac{LiCl}{AgCl}$.	Atomic weight of Li. Ag = 107.880.
14	C	6.28662	21.25442	0.295779	6.9391
15	C	5.82076	19.67873	0.295790	6.9407
16	C	6.70863	22.68030	0.295791	6.9409
17	C	6.24717	21.12073	0.295784	6.9399
18	C	5.50051	18.59600	0.295790	6.9407
21	E	8.34521	28.21438	0.295779	6.9391
22	E	6.65987	22.51564	0.295789	6.9406
		45.56877	154.06020	Av. = 0.295786	6.9401

Comparison of these results is highly interesting, and leaves no doubt concerning the atomic weight of lithium. The average result for the atomic weight of lithium, computed from these final results taken together, is 6.9401, with a "probable error" of 0.0002.

It is pleasing to note that the average, 6.9403 of experiments 14 to 18 inclusive, made with sample C of lithium chloride is almost identical with the average 6.9399 of experiments 21 to 22 made with Sample E. The difference between the averages is only 0.0004, and the average of the first five lies between the values given by the last two experiments. The extreme range is only from 6.939 to 6.941, whereas the extreme range in the preliminary series was from 6.938 to 6.945.

The agreement of these two samples made from different raw materials and purified in somewhat different ways seems to leave no doubt concerning the validity of the result except insofar as constant errors in the methods of analysis or constant unavoidable impurities are concerned. The former of these causes of uncertainty is rendered highly improbable by the next series of experiments, to which attention is now directed.

The Ratio of Lithium Chloride to Silver.

A single series of experiments is never convincing in work of this kind; accordingly the preceding determinations were supplemented by others, which determined the exact amount of silver necessary to precipitate the chlorine in weighed amounts of lithium chloride. No important difference in the final value was expected, because sodium and potassium showed none under similar conditions, but the further work had the advantage of making "assurance doubly sure."

In this series of experiments weights of the purest silver, equivalent to those of the lithium chloride, as calculated from the preceding table, were dissolved in nitric acid in a Jena flask provided with a tower of bulbs to prevent loss by spattering. Almost the exact amount of silver could be weighed out directly, by selecting suitable pieces from a large assortment of very fine globules; and the last few hundredths of a milligram were added, if necessary, in the form of a standard solution, prepared from the same silver. The solution of silver nitrate was diluted to about 1 liter and added to the solution of lithium chloride exactly as in the preceding series. Great care was used to transfer every trace of silver from the flask. After standing for a day or two, with occasional violent shaking, the presence of an excess of silver or of chlorine was then determined with the nephelometer, following the procedure adopted by Richards and Wells.[1]

One very important innovation was introduced. The accuracy with which the end-point can be determined by this method is almost inversely proportional to the concentration of the silver halide remaining in solution, because the percentage accuracy of the nephelometer does not increase with increasing cloudiness. It has long been recognized that the titration of bromides is more exact than that of chlorides, because the solubility of silver bromide is less than one-tenth of that of the chloride. These considerations show that any means of decreasing the solubility of silver chloride will increase the precision of the end-point. The solubility of silver chloride in water changes greatly with the temperature,[2] being over four times as great at 34° as it is at 1.5°. It seemed worth while, therefore, to try the effect of cooling the solution in ice. Analysis 3 was made to test this point. At this time the weather was quite warm, the temperature sometimes rising above 30°. The solubility was tested on fourteen successive days, the flask being shaken each day. It was found to vary from 2.2 mg. to 3.4 mg. per liter; the presence of nitric acid was undoubtedly responsible for a higher average value than Kohlrausch's. Opalescences produced by the precipitation of the chloride in such a solution are so intense that it is difficult to estimate accurately their contents in the nephelometer. The flask was then packed in ice, and the solubility again determined for several days. It became very constant, varying from 0.5 to 0.6 mg. per liter. Most of the values obtained were about 0 5 mg., a figure which begins to be comparable with that for silver bromide at ordinary temperature—0.10 mg. The opalescences were so faint that the slightest excess of silver or of chlorine was unmistakably evident. Richards and Wells estimated that they could detect a difference of 0.02 mg. of silver per liter; this limit we have doubtless reduced by cooling. Assuming the weight of lithium chloride to have been accurate to within 0.02 mg., there could not have been an error exceeding 0.05 mg. in the weight of silver, since the total volume was only two and one-half liters. The determination by this new method of the weight of silver required is evidently the most accurate part of the analysis, and the cause of the variation in results must be sought elsewhere. There is moreover another advantage in this method. Since the concentration of silver chloride in solution is constant, at the constant low temperature, it is possible to calculate with greater exactness than before the amount of a deficiency of either silver or chloride, in terms of the ratio of lengths of the two nephelometer columns giving equal apparent opalescences. This advantage hastens the work.

---

[1] This Journal, 27, 502 (1905).

[2] Kohlrausch, *Z. physik. Chem.*, 64, 148 (1908).

Only two preliminary experiments were made, for the technique required by the determination is so simple that it is readily mastered. The results of these two preliminary experiments, made with material not perfectly free from sodium, are given below:

RATIO OF LITHIUM CHLORIDE TO SILVER.

Preliminary Series.

No of experiment.	Continuation of analysis.	Preparation of LiCl.	Wt fused LiCl, vacuum.	Wt. of Ag, vacuum.	$\frac{\text{LiCl}}{\text{Ag}}$.	Atomic wt. of Li. Ag = 107.88.
23	3	A	8.99620	22.89013	0.393017	6.942
24	7	B	5.25395	13.36777	0.393030	6.943
				Average,	0.393023	6.942

The results agree almost exactly with the preliminary experiments made by the other method with similar material, as may be seen by referring to the first table on page 30. As has been said, these preliminary experiments are, of course, entirely neglected in this comparison of final results. All of the preparations used in this preliminary work contained traces of sodium, which would, of course, raise the apparent atomic weight of lithium; and accordingly these early values if included in the calculation would introduce a source of error. The experiments were, nevertheless, of great value to the investigators in the course of the work; therefore they seemed worthy of brief notice.

After the various processes had been mastered, the final series, using utmost care to exclude all sources of error, was undertaken. The exper-

RATIO OF LITHIUM CHLORIDE TO SILVER.

Final Experiments.

No. of analysis.	Continuation of analysis No.	Preparation of LiCl.	Wt. fused LiCl, vacuum.	Wt. Ag, vacuum.	$\frac{\text{LiCl}}{\text{Ag}}$.	Atomic wt. of Li, Ag = 107.88.
25			5.82422	14.82035	0.392988	6.9386
26	14	C	6.28662	15.99687	0.392991	6.9389
27	15	C	5.82076	14.81122	0.392997	6.9396
28	16	C	6.70863	17.07038	0.392998	6.9397
29	17	C	6.24717	15.89620	0.392998	6.9397
30	..	C	7.75349	19.72977	0.392984	6.9382
31	..	E	7.99108	20.33415	0.392988	6.9386
			46.63197	118.65894	0.392992	6.9390

iments were consecutive. The method is simple, and accident easily avoided. Four experiments (Nos. 26 to 29 inclusive) were utilized further by weighing the precipitated silver chloride. This portion of the experiment received in each case another number, and the results are given as experiments 14 to 17 inclusive in the table on page 31.

These experiments then point to the number 6.9390 as the atomic weight of lithium, a number possessing a so-called "probable error" of less than 0.0002. It will be observed that the maximum deviation from the mean of all the experiments was less than 0.001 in the atomic weight of lithium, a quantity which corresponds to only about one part in 65,000 of the lithium chloride. This is about as high a grade of accuracy as has usually been attained in atomic weight work. It means about one-tenth of a milligram in weight of the substance taken, although the error is probably not to be traced to the work but rather to inevitable complications in the chemical part of the various processes, especially to occlusion of soluble salts by the silver chloride.

Discussion of the Final Results.

Thus two final results have been obtained for the atomic weight of lithium, namely, 6.940 by reference to silver chloride, and 6.939 by reference to pure silver. The close agreement of these values is important evidence of their verity, and there seems to be no doubt that the value 6.94 may be taken with great certainty as representing the true atomic weight of this lightest of the metals, supposing that silver is called 107.88. A change of 0.01 in the atomic weight of silver causes a corresponding change of only 0.0006 in that of lithium.

The reasons for the higher atomic weight found by other experimenters are not far to seek. Stas admitted that his lithium chloride was alkaline, a circumstance which would, of course, have raised the apparent atomic weight, and it is probable that further error was introduced by other impurities. Judging from the difficulties encountered in the present work, his methods of purification must have been entirely inadequate. In those cases in the work of others where the approximately correct value of lithium had been found, the fortunate result must be attributed rather to a compensation of errors than to any special excellence.

The fact that the two series of results gave essentially the same atomic weight of lithium shows that they indicate very nearly the same atomic weight of chlorine, referred to silver, as that found in the work of Richards and Wells. The average of the present work shows that one part of pure silver would give $\frac{0.392992}{0.295786} = 1.32864$ parts of chloride, while Richards and Wells obtained 1.32867. This shows that the silver must have been pure within one part in forty thousand, a fraction about equal to the experimental error of the analysis. One pair of experiments, namely the pair numbered 16 and 28, gave exactly the value found by Richards and Wells.

Another method of comparing these results is to reduce them both to the ratio of lithium chloride to silver. On this basis, if one part of silver chloride corresponds to 0.295786 of lithium chloride, and one part of silver corresponds to 1.32867 parts of silver chloride,[1] then one part of silver must correspond to 0.393002 part of lithium chloride. This obviously differs by one part in 40,000 from the result 0.392992 found directly. The mean of these two figures, namely 0.392997, may perhaps be supposed to represent the true value of the ratio to within one part in 80,000. This value will be chosen for the computation involved in the subsequent work.

Summary.

In conclusion of the first part of the work, the following brief summary presents the chief features. Lithium salts were in the first place studied with great care in order to discover the most suitable substance for the investigation and the best methods of purifying them. The precipitation of lithium as fluoride and the conversion of this precipitate into nitrate or perchlorate with many recrystallizations of the soluble salts was found to be the surest method of eliminating impurities, especially sodium. The perchlorate was decomposed by heat; the nitrate precipitated by ammonium carbonate in order to convert it into chloride. The purer the material the lower was the observed atomic weight of lithium, and the two purest samples gave precisely the same results within the limit of error of experimentation. In all 46.56877 grams of lithium chloride yielded 154.0602 grams of silver chloride, corresponding to 6.940 as the atomic weight of lithium. Moreover, 46.63197 grams of lithium chloride were found exactly to precipitate 118.65894 grams of silver, corresponding to the value for the atomic weight 6.939. These essentially identical results may be taken to represent the atomic weight of lithium, if silver is taken with the International Committee to be 107.88. If each of these results is given equal weight and 100.000 parts of silver are assumed to produce 132.867 parts of silver chloride, the corresponding amount of lithium chloride is 39.2997 parts.

PART II.—THE RATIO OF OXYGEN TO LITHIUM CHLORIDE.

Preliminary Experiments.

The reasons which led to the selection of lithium perchlorate as the salt to be used in determining the ratio between oxygen and silver, and the advantages of this substance, have already been mentioned briefly in the introduction. Part I of this paper[1] has described the determination of the atomic weight of lithium—an essential link in the chain of data.

---

[1] Richards and Wells, *Publ. Carnegie Inst. of Washington*, 28, 65 (1905).

After lithium perchlorate had been found to be susceptible of fusion without decomposition—thus being rendered anhydrous and suitable for accurate weighing—a method had to be devised for obtaining experimentally the ratio of perchlorate to chloride, and hence the ratio of oxygen to the chloride and to metallic silver.

Naturally, the first attempts were directed toward the quantitative conversion of perchlorate into chloride. Simple ignition first suggested itself, but was quickly abandoned, because this process involves a loss of chloride, unless extraordinary precautions are taken. The oxygen evolved carries with it particles of the salt so extremely minute that they color a flame fifteen or twenty feet distant, if the operation is performed in an open dish. To retain this dust would require such an elaborate apparatus that accurate weighing would be out of the question.

A means of reducing the perchlorate was then sought, which would prevent this evolution of oxygen, but this proved futile, for, as Kreider has shown,[2] perchloric acid is, in combination, one of the most stable of the oxygen acids, and is hardly affected even by the strongest reducing agents. Hydrogen is entirely without action on the fused salt at 300°, and hydrochloric acid was found to displace only very little of the perchloric. In aqueous solution the situation is not much more promising. Although chlorates in solution are readily reduced, perchlorates under the same conditions are almost entirely unaffected by the most powerful reducing agents, with the exception of ferrous hydroxide and titanous salts, which, in large excess, and upon long boiling, reduce them to chlorides.[3] This method is, however, quite unsuitable for precise work. All attempts to convert perchlorate into chloride, therefore, had to be abandoned, and the reverse process was considered.

The vapor from a constant-boiling mixture of perchloric acid and water, both alone and mixed with additional steam, was passed over lithium chloride at different temperatures; but although some hydrochloric acid was expelled, the conversion into perchlorate was only partial. Frothing and creeping occurred, with unavoidable loss of material. The anhydrous acid was not tried, for its use is highly inconvenient or even dangerous; and after an examination of the thermochemical relations involved, there was no reason for supposing that it would be any more effective than its hydrate, which has a higher boiling point. Recourse was had, therefore, to a method similar to that used by Richards and

---

[1] See the preceding pages.

[2] *Am. J. Sci.*, 50, 287 (1895); *Z. anorg. Chem.*, 10, 277.

[3] Sjollema, *Z. anorg. Chem.*, 42, 127 (1904). Rothmund, *Ibid.*, 62, 108 (1909).

Forbes[1] in the synthesis of silver nitrate. Lithium chloride was dissolved in water in a quartz flask, a slight excess of perchloric acid was added, over and above the amount needed to convert the salt wholly into perchlorate, and the solution was evaporated by allowing a current of air to pass through the flask, the temperature being regulated so that no ebullition occurred. The hydrochloric acid was soon expelled, and by gradually raising the temperature the excess of perchloric acid was volatilized, leaving pure, fused lithium perchlorate. The substances in the flask were thus changed gradually from a solution of the chloride into pure fused perchlorate, without the formation of a single bubble of gas or vapor. Hence the process is capable of the greatest accuracy.

Further experiments, planned in order to test details of the operation, showed that pure, neutral perchlorate, prepared by recrystallization, could be heated to 300° without decomposition. On the other hand, the salt formed in the above process always contained a trace of chloride and chlorate—as shown by its giving off oxides of chlorine when moistened with perchloric acid. This small amount, however, did not increase on further heating—a fact which indicated that it must have been formed during the evaporation of the excess of acid. This train of circumstances suggested that the impurities might be due to a decomposition of the last traces of acid, which are evolved only at a high temperature and in a nearly anhydrous condition. Since the anhydrous acid decomposes readily, while the dihydrate is very stable, it seemed reasonable to suppose that if the last traces of acid were removed at the lowest possible temperature, and in a current of air saturated with moisture (to prevent the dissociation of the dihydrate), this decomposition ought to be prevented, and a salt almost, if not quite, free from chloride obtained. This was found to be true. The purity of the perchlorate obtained depends upon the care with which the excess of acid is expelled before the temperature attains a high point.

The Conversion of Lithium Chloride into Perchlorate.

The determination of the ratio of lithium chloride to oxygen thus resolved itself into the following processes: Lithium chloride was to be fused and weighed in a boat just as described in Part I; it was then to be dissolved in a slight excess of perchloric acid; the hydrochloric and perchloric acids were to be driven out by steam; and the fused perchlorate was to be dried at 300° and finally weighed. The gain in weight of the salt is caused by oxygen alone and gives at once the ratio O_4 : LiCl. From the known ratio of lithium chloride to silver, the atomic weight of the last-named element is to be calculated.

The general method having been indicated, the complete details of the operation and the apparatus used will now be described. The preparation of very pure perchloric acid and lithium chloride has been already discussed in Part I.

---

[1] THIS JOURNAL, 29, 808 (1907).

The quartz flasks, of 100 cc. capacity, which served to conduct the quantitative evaporation, were made especially for the work of Heraeus. They are shown in cross section in Figures 3 and 4, and may be called evaporating flasks.

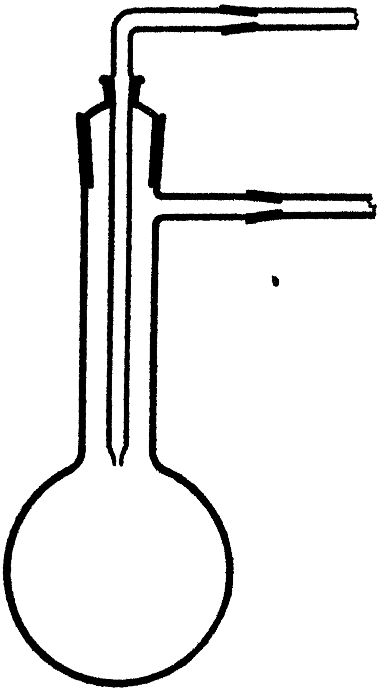


Fig. 3.

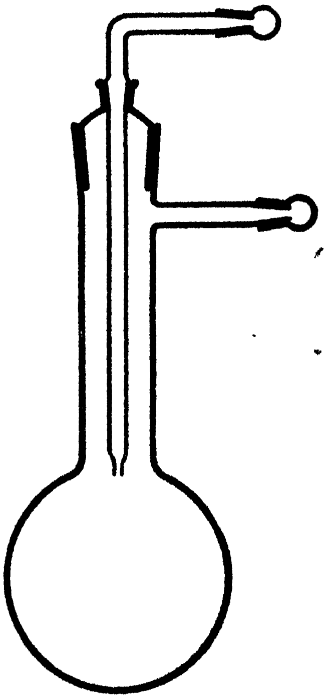


Fig. 4.

The quartz stopper was provided with a ground joint, into which fitted the bent quartz delivery tube. This tube could be removed and replaced by a small quartz stopper if desired. The ends of the delivery and exit tubes were ground to fit glass tubes (as in Fig. 3), which were attached during the evaporation, and after the operation was finished, were replaced by glass caps, which effectually closed the flask (Fig. 4). A loop of platinum wire fastened around the neck of the flask served to suspend it from the balance while it was being weighed. One of the flasks was used as a counterpoise. They were kept in separate large Hempel desiccators, with sticks of potassium hydroxide, and supported on baskets of platinum wire. Before weighing the empty flask it was always heated to 300° and dry air was passed through it for a short time, in order to remove any adsorbed moisture, and the flask then allowed to cool in a desiccator. As a matter of fact, experiment showed the same weight was obtained if the flask was filled with dry air at the ordinary temperature, but as a precaution it was always heated.

Platinum seemed to accelerate the decomposition of perchlorate by heat, as might have been expected, and the presence of this metal was, therefore, to be avoided. Hence it seemed desirable to fuse the lithium chloride, the accurately weighed factor in the reaction, in a quartz boat, which could then be left in the evaporating flask during the subsequent conversion to perchlorate. The troublesome transfer of its contents would thus be avoided. Careful quantitative experiments showed the lithium chloride could be fused in quartz in a current of hydrochloric acid without attacking the boat in the least, but unless the walls were very strong, it was cracked by the contraction of the fused salt as it cooled. A heavy-walled boat meant a smaller capacity for the fused chloride, and since it was desired to employ the maximum possible amount, the use of quartz was abandoned. A boat of platinum-iridium was especially made to fit into the flask, and used thereafter for the fusion of the lithium chloride. At one end was a slight projection provided with a hole, through which was passed the platinum wire that served to lower the boat into the flask.

The fusion and weighing of the lithium chloride have already been described in the first part of this paper, and need only be referred to here. The boat containing the fused and carefully weighed chloride was lowered gently into the neck of the evaporating flask to which had just been added a few cubic centimeters of purest water direct from the still. The flask, with the boat suspended in the neck, was placed over an electric heater, covered by a large bell-jar and kept warm over night. The aqueous vapor condensing on the chloride dissolved it, and the solution flowed down into the bulb of the flask. If time were an object, the boat was lowered directly into the water and the contents dissolved in a few minutes, but this method required more water than the other. In either case the final washing was accomplished as follows: To a wash-bottle was attached a glass tube terminating in a capillary, bent sharply at the end at right angles and cut off so close that it was very little thicker than the rest of the capillary and could be passed between the boat and the walls of the flask. By means of this fine horizontal jet of water, the boat could be washed on all sides and within. Since the wash-bottle was of Jena glass, and the water was allowed to remain in it only a few minutes, no appreciable amount of alkali could have been introduced in this way.

The boat was then lifted out and carefully rinsed in a beaker, the washings being tested in the nephelometer for chloride. The amount found was never more than a few hundredths of a milligram. This correction, when appreciable, was applied to the weight of lithium chloride.

A slight excess of the purest perchloric acid, which had been condensed and collected entirely in quartz, was now added. The contents of the evaporating flask were thoroughly mixed, and the flask was placed on a support of platinum wire in an electric oven. The oven was made especially for this purpose by winding a three-liter beaker with resistance ribbon, a window being provided through which the flask within could be observed. The stopper and delivery tube were inserted into the flask, and the delivery tube was connected by a ground joint with the source of moist air. The exit tube, passing through a hole in the side of the oven, was connected with a water pump to remove the acid vapors. The oven was provided with a glass cover, suitably perforated to admit the thermometer and the delivery tube.

The air, supplied by a water pump, was purified by passing successively through towers, some containing potassium hydroxide solution with a little manganate, and others containing a fifty per cent. solution of phosphoric acid, to which had been added potassium permanganate. Thus the air was freed from soluble impurities.

When dry air was desired, the current was passed through further tubes containing, respectively, fused potassium hydroxide and resublimed phosphorus pentoxide. When moist air was desired, it was passed through an electrically heated gas washing bottle containing water. By turning the proper stopcocks either moist or dry air could be passed into the evaporating flask. To prevent the condensation of water in the tube, the latter was wound with resistance wire from the bottle as far as the point connecting it with the quartz flask, and heated by the passage of a suitable current. The temperature of the oven containing the evaporating perchlorate solution was read on a thermometer, the bulb of which was placed in contact with the evaporating flask as close to the fused salt as possible.

The temperature of the oven was kept at 130° while dry air passed through the flask until about two-thirds of the water had evaporated; then it was raised to 150° until most of the hydrochloric acid had been expelled. Moist air was at this stage passed through the evaporating flask, and soon perchloric acid was evolved. After several hours at 160° no more appeared; at 180° a little more was expelled, and from this point the temperature was slowly raised to 250°. The salt was then neutral but not quite anhydrous. To remove the last traces of water, it was heated in dry air at 280–300° for at least five hours; further heating was found to cause no diminution in weight. The entire operation usually occupied three days. The perchlorate was allowed to cool in the current of dry air, until the crystals began to appear. It was then warmed to the freezing point (236°) and allowed to cool very slowly, so as to avoid too violent solidification. It was quite crystalline and transparent. The glass caps were then placed over the ends of the tubes and the flask was quickly removed to the desiccator, which was placed for a sufficient time beside the balance case in a room kept at nearly constant temperature.

The possibility that solid material which ought to be weighed might be carried away with escaping gas and vapor during the evaporation was duly considered. Experiments already made with silver nitrate[1] make it unlikely that this was the case. The method of evaporation seems to be really quantitative. Nevertheless, although no mechanical loss is apparent, there is a conceivable possibility that traces of the lithium perchlorate might be carried away in the state of vapor with the escaping perchloric acid or water at the high temperature. Unlikely as this might seem, it is nevertheless worth testing, and the test was easily applied by adding perchloric acid and water after the fused substance had been weighed and then repeating the evaporation, fusion, and weighing. The interpretation is somewhat complicated by the fact that the true weight of perchlorate can never be attained with perfect accuracy until one knows how large an amount of chloride and chlorate have been formed during the fusion. Rarely were these impurities wholly absent. Nevertheless, the following test is fairly satisfactory.

A neutral solution of nearly 14 grams of pure lithium perchlorate, after various preliminary trials in order to find the best succession of temperatures for the evaporation, was treated with a few drops of an excess of perchloric acid, and the acid was evaporated at 165° for several hours until the mass solidified. The temperature was now raised to 200° and kept there until the mass which had partially melted had again solidified; again gradually raised to 245°, and kept there for less than two hours; yet once more gradually raised to 280° where it was kept for five hours, and finally to 300° for yet three hours more. After making the correction to vacuum, the lithium perchlorate was found to weigh 13.92425 grams. It was then heated to 300° for five hours more and lost 0.00025 gram. This loss was due to loss of oxygen, however, as shown by the fact that on adding dilute perchloric acid a pale yellow solution was obtained. This was again evaporated rapidly at about 210°. Gradually the temperature was raised to 240° and was kept there until the excess of acid had been expelled and was then heated to 300° for three hours. The weight was now 13.92419, or only 0.00006 less than the first weight. As the heating had been brief, it was continued at about 300° for four hours more, when the weight was found to be 13.92416, essentially the same as before. Upon being dissolved in very dilute perchloric acid no trace of yellow color was observable, showing that the substance this time had not been greatly decomposed. Nevertheless, in order to test the matter yet again, the fused salt was dissolved in very dilute perchloric acid once more.

---

[1] THIS JOURNAL, 29, 815 (1907).

The water and perchloric acid were driven off as before, and the residual salt was dried three and a half hours at 300°. This time again the weight had changed only one-thirtieth of a milligram, being 13.92413 grams; and upon dissolving in dilute acid no trace of yellow color was to be perceived. Thus the total loss in two evaporations amounted to only 0.00012 gram, or an average of about one-twentieth of a milligram for each evaporation. This small loss is negligible, being only 1 part in 200,000 of the weight of material in question, and even this may be due to nothing more than a slightly greater loss of oxygen before the last weighing than before the first. An accident prevented the determination of the amount of chloride in the final sample. In the carefully finished determinations given in the final table the amount of oxygen lost varied from 0.00009 gram to 0.00078 gram, or on the average about 0.0004 gram. This is considerably more than the divergence between the weights given above, and therefore it is clear that the agreement noted above is as good as could be expected, and shows that no important amount of material is carried away with the stream of vapor and air during evaporation.

The Weighing of Lithium Perchlorate.

When perfectly neutral, lithium perchlorate is not in the least deliquescent in air of ordinary humidity, but the presence of a very little acid suffices to make it so. After several days' exposure the pure salt is still apparently dry. Nevertheless, great care was taken not to expose the contents of the evaporating flask to the air. The ground stoppers of the flask were always kept closed, and although they were not quite as tight as those on the weighing bottles for the lithium chloride, they were evidently sufficient for the purpose.

In order that the apparent weight of lithium perchlorate might be corrected to a vacuum standard, the density was found by determining the weight of toluene displaced by a known quantity of salt. The toluene had been dried over sodium and then distilled. Its density at 25° referred to water at 4° was found to be 0.8617. Pure lithium perchlorate was fused in a quartz crucible in a current of dry air, broken into coarse pieces and transferred to an Ostwald pycnometer, modified for use with solids. Great care was taken to remove all air bubbles by shaking in a vacuum. The following table records the results:

DENSITY OF LITHIUM PERCHLORATE.

Weight of $LiClO_4$ in vacuum, grams.	Weight displaced toluene in vacuum.	Density of $LiClO_4$ 25°/4°.
5.2866	1.8757	2.4285
5.2866	1.8760	2.4283

The mean value is 2.428, and assuming the density of the weights as 8.3, a correction of 0.0003501 gram was added to every apparent gram of lithium perchlorate.

The weighing of the evaporating flask with its counterpoise proved to be rather troublesome. During the first few minutes on the balance, the flask lost somewhat in weight, frequently as much as 0.20 mg.; but eventually the weight became constant. Since both flasks showed this behavior it was not a serious matter, for constancy with respect to one another was all that was required. After waiting until constancy had been reached, the weight of the flask obtained after replacing it a second time upon the balance was usually within a few hundredths of a milligram of the first one. The initial irregularity may have been due to adsorbed moisture, but was more probably due to slight temperature changes, for with so large a vessel half a degree Centigrade would cause this difference. Hence the temperature of the balance case and the flasks should not change appreciably during the weighing; the more nearly this condition was realized, the more accurate was the result. A large pane of glass was placed between the observer and the balance to prevent the heat of the body from reaching it.

Impurities in the Fused Perchlorate.

There could have been only four possible impurities in the salt (provided that the lithium chloride and the perchloric acid and water were pure, and that the vessels were not attacked), namely, chloride, chlorate, hydroxide and water. The tests for these will be discussed in order.

After the flask had been weighed, its contents were dissolved in 0.1 liter of water, and the chloride present in 25 milliliters was determined in the nephelometer. The amount was always small—usually less than 0.002 per cent.—and the corresponding correction averaged about four-tenths of a milligram in 14.3 grams of perchlorate. The following table contains a statement of the amounts of chloride found in each of the final experiments, and a correction which was applied to the final weight of lithium perchlorate containing these impurities in order to allow for the oxygen lost. It is evident that for every 0.425 milligram of lithium chloride found, 0.64 gram of oxygen must have been lost, these quantities being in proportion to the combining weights. In the last determination, involving over 22 grams of perchlorate, the correction was so small as to be practically negligible; and in only one or two cases, in which the heating had probably been somewhat too rapid, did the total correction amount to any serious quantity.

Traces of chlorate were always likely to be present with the chloride, and since the quantity was very small, it was most conveniently estimated nephelometrically after reduction with a solution of pure sulphur dioxide. This gave the total chloride, the amount corresponding to the chlorate being obtained by subtracting that previously found as chloride. The correction for chlorate was usually entirely negligible; its amount was determined in four cases, analyses 1, 2, 7 and 11. Only in the last of these cases where the amount of lithium chloride found was unusually large did the necessary correction equal one-twentieth of a milligram; it was usually less than one-thirtieth. As a rule the more chloride present, the greater was the amount of chlorate, although the proportionality was not exact. Because one-twentieth of a milligram was only one part in 300,000 of the weight of perchlorate in the case of Experiment 11, and the amount present did not exceed this fraction in any of the other cases, the correction might have been entirely neglected without introducing appreciable error.

No. of experiment.	Weight of LiCl found. Milligram.	Correction applied to weight of $LiClO_4$. Milligram.
7	0.13	+0.20
8	0.50	+0.75
9	0.16	+0.24
10	0.21	+0.32
11	0.52	+0.78
12	0.06	+0.09

The formation of alkali was never observed, the solution of the perchlorate being always absolutely neutral to indicators. Even when the salt is *completely* decomposed into chloride, only a little oxide or hydroxide is formed, and in the specimens obtained in this work where only a trace of any kind of decomposition occurred, the amount of alkali must have been infinitesimal indeed.

Although it seemed probable that the salt dried under these conditions was perfectly anhydrous, the inference could only be verified by complete decomposition, as in the corresponding work of Richards and Forbes on silver nitrate. Lack of time has thus far prevented the completion of this final test, but a comparison of our work with the results of these authors indicates that the amount of water, if any, must be extremely small. They found certainly not over 0.001 per cent. in silver nitrate dried one hour at 210°, while the lithium perchlorate was heated to 300° for four or five hours in perfectly dry air. The correction for 0.001 per cent. of water in the perchlorate would raise the atomic weight of silver only 0.002.

Valuable information concerning the probably anhydrous nature of the salt, corroborating the above conclusions based on analogy, was actually obtained in four cases. During the progress of analysis 8 the lithium perchlorate was heated in the first place for four hours at 280°. Three hours more at about the same temperature caused a further loss of only 0.19 milligram, or 0.002 per cent. This loss, being much less than the weight [illegible] oxygen lost by the substance, may have been entirely due to the incipient decomposition. At any rate, even supposing the loss had been due to water, one might well infer that further heating could hardly expel more than 0.1 of a milligram additional. As will be seen, this inference was verified later. The ninth experiment was treated in dry air for six hours at 252°, a temperature at which the water would undoubtedly be expelled much less rapidly. Two and a half hours more at a temperature 30° higher caused the expulsion of about 0.2 milligram, and yet three hours more at the same temperature caused a further loss of but little more than 0.1 milligram. Thus only 0.003 pr cent. of the weight of the salt dried at 252° was lost by prolonged heating at 285°. Even this loss may have been due chiefly to oxygen, of which 0.24 milligram was shown to be lacking by the presence of 0.16 milligram of lithium chloride in the product.

In Experiments 11 and 12 higher temperatures were used. After having been dried for four and a half hours at 290–300°, the lithium perchlorate in this experiment weighed 17.84843 grams, and after further drying in a current of pure dry air for three hours at 300°, it weighed 17.84842, a loss of only 0.01 of a milligram. It seemed unlikely that further heating even at this high temperature would cause any further loss of weight. The last experiment, No. 12, was the most conclusive of all. The salt was first dried for five hours at 280° and was found to weigh 22.58271 grams. After three hours further heating at 280°, three hours more at 300°, and a few minutes at 310°, the specimen weighed 22.58275, a slight *gain*, but one not exceeding a possible error of weighing. Further heating for one hour at 300° caused an opposite change of only one-thirtieth of a milligram in this salt. The weight accepted as the true one was 22.58273, and one can hardly believe that this substance still retained an appreciable amount of water. These weighings demonstrated not only the probable absence of water, but also the striking stability of the salt.

The four impurities which might possibly have come from the pure materials employed have thus been discussed in detail. It remains to consider the impurities which might have come from the vessels used and from the gases in contact with the fused materials.

The lithium chloride (forming the starting point of the determination) was fused in a platinum boat. In most of the experiments this boat was weighed before and after the fusion, and was usually found to have lost but little. For example, in Experiment 7 the loss was 0.02 milligram, and in Experiment 8, 0.05 milligram and in Experiments 9 and 10, taken together, only 0.01 milligram. Thus in four experiments involving the fusion of over 18 grams of lithium chloride the total loss of weight was only 0.08 milligram, or 0.0004 per cent. of the weight of the lithium chloride. On the other hand, in the last experiment, No. 12, which was otherwise the best of all, the boat lost much more in weight, because in this case a new boat had been employed to accommodate the unusually large quantity of material. The loss was here 0.3 milligram. There was every reason to believe, because in other cases the platinum was not attacked, that this excessive loss, amounting to 0.003 per cent. of the lithium chloride, was due, at least in part, to iron volatilized from the boat during fusion at high temperature in hydrochloric acid. The boat had indeed been previously cleansed by treatment with ammonium chloride at high temperatures as usual, but apparently the cleansing had been insufficient. The mean weight of the boat was taken as the true one. Even the maximum error resulting from this choice amounts to only one part in 60,000 of the weight of lithium chloride, a quantity which seems often to represent the limit of accuracy in experimental work of this kind. On the whole, the evidence is that the boats were not sufficiently attacked to cause any important constant error in the series of results.

Turning now to the quartz flask, the only other receptacle used during the experiments, it was easy to prove that this was not appreciably attacked during the experiments. In three cases in which no regrinding of joints or alteration in tare weight had been necessary, the following successive tares of the evaporating flask were found: Experiment 8, 0.00106; Experiment 9, 0.00103; Experiment 10, 0.00104. This practically proves that the flasks were not appreciably attacked by the acid lithium perchlorate at 300°. It is of course possible that the flasks gained from the fused mass a weight of lithium equal to the weight of silica dissolved, but this is unlikely, especially because the flasks to-day, after all the determinations, still appear perfectly clear and transparent as they did at first.

Neither sodium chloride, silver chloride, nor silver nitrate were found in the previous investigations[1] to retain on fusion perceptible amounts of oxygen or nitrogen or argon, and, as the air and nitrogen passed over the lithium chloride and lithium perchlorate in the present experiments were both free from other gases, it is reasonable to infer that these salts also did not contain dissolved gas. The absence of hydrochloric acid from the lithium chloride which had been fused in the gas, and subsequently while fused heated in a current of pure nitrogen, was proved by complete neutrality of the dissolved product.

From these considerations it would appear that both the lithium chloride and lithium perchlorate were obtained in these experiments in a state of purity as great as is practicable in the present state of work of this kind, and therefore that the conclusions based upon the quantitative results are inferior to none.

[1] Richards and Wells, *Publ. Carnegie Inst. Washington*, 28, 55, 60 (1905). Richards and Forbes, *Ibid.*, 69, 55 (1907).

There follows a table containing the four preliminary results which were brought to a satisfactory conclusion. The third and sixth of this preliminary series were vitiated by known experimental errors, due to inexperience with the processes involved. No great accuracy is claimed for these results, but they serve to show that the process was one which was capable of exact work, and afforded the valuable training needed to carry out the six consecutive final experiments which followed. The lithium chloride used in these preliminary experiments was not perfectly pure, being of the same quality as that used in the preliminary experiments of the other series. In calculating the last two columns of the table below, values for the ratio LiCl : Ag were chosen which corresponded with the particular samples of slightly impure lithium chloride used in each case, namely, 0.39298 for Experiments 1 and 2, and 0 39304 for Experiments 4 and 5. Thus a large part of the error due to impurities in the lithium chloride was eliminated:

RATIO OF OXYGEN TO SILVER, O_4 : Ag.

Preliminary Series

No of experiment.	Sample of salt.	Weight fused LiCl. vacuum.	Weight fused $LiClO_4$. vacuum.	$\frac{4O}{LiCl}$.	$\frac{4O.}{Ag}$	Atomic wt. of Ag.
1	O	4 24171	10 04596	1.50983	0.59333	107.87
2	O	5 09073	12 77683	1.50982	0 59333	107.87
4	D	4.03587	10.12750	1.50957	0.59324	107.88
5	D	5.19638	13.04021	1.50948	0.59329	107.87
				1.50962	0.59330	107.872

Thus the atomic weight of silver is shown by these preliminary results to be not far from 107 872. It is interesting to note that if Stas's value for the relation of lithium chloride to silver had been used in making the computation of these results, the atomic weight of silver recorded in the last column would have been 107 70. This value is quite impossible in view of results obtained in other ways, and serves to emphasize the grave error which unquestionably existed in Stas's work on lithium chloride.

These preliminary experiments having furnished an adequate preparation for the execution of an exact series of experiments, six syntheses yielding the following results were made. The lithium chloride used in the determinations was preparation C already used in previous work involving the comparison with silver. The advantage of using similar material in the two sets of experiments has already been emphasized. Every precaution was taken, and, although we feel that with the experience gained in these experiments, a yet more consistent series might be obtained, especially if somewhat larger quantities of material were used; nevertheless, it is evident that this degree of accuracy will not be easy to exceed.

The following table explains itself. The weight of lithium perchlorate given was in each case obtained by adding to the actual weights (corrected to the vacuum standard) the corrections for chloride given in the last column of the table on page 44, together with the vanishingly small corrections for chlorate mentioned just afterwards. In calculating the values given in the last and next to the last column, the ratio of lithium chloride to silver is assumed to be 0.392997 : 1 as previously stated at the conclusion of Part I. No experiment was rejected.

THE RATIO OF OXYGEN TO SILVER. O_4 : Ag.

Final Series.

No. of experiment	Weight fused LiCl (vacuum).	Corrected weight fused $LiClO_4$ (vacuum).	$\frac{4O}{LiCl}$.	$\frac{4O}{Ag}$.	Atomic wt. of silver.
7	5.09744	12.79265	1.50962	0.593276	107.876
8	4.20534	10.55416	1.50970	0.593307	107.876
9	4.54205	11.39912	1.50769	0.593302	107.871
10	4.45070	11.17008	1.50974	0.593323	107.867
11	7.11167	17.84842	1.50974	0.593323	107.867
12	8.99846	22.58273	1.50962	0.593276	107.876
	Sum. = 34.40566	86.34716	Av. = 1.50968	0.593301	107.871

Thus, according to this series of results, silver is 107.871, if oxygen is taken as 16.000, and the ratio of lithium chloride to silver is taken as 0.392997 : 1. A variation of 4 in the sixth decimal place of this latter ratio would cause a change of only 0.001 in the atomic weight of silver. There seems to be no doubt that the ratio of lithium chloride to silver is not much more in error than this, and accordingly that the atomic weight of silver given by this series of results is free from error due to the work described in the first part of the present paper. The probable error of the final result, 107.871, according to the method of least three squares, is 0.003. The only possibility of serious uncertainty seems to lie in the possible retention of water by the fused lithium perchlorate. This would obviously tend to make the atomic weight of silver appear lower than it is. Accordingly we are disposed to believe that the value 107.871 represents the lower limit. The last analysis, made with the largest amount of material and showing the least decomposition, was probably the most satisfactory determination of all, and it will be noticed that in this case the value is somewhat higher than the average. If silver is 107.871, lithium becomes 6.939, essentially the same as if silver were 107.88. Chlorine is somewhat more affected by this difference in silver, sinking from 35.457 to 35.454.

Further determinations carried out as this last determination was, together with other experiments in which the possible presence of water remaining in the final substance should be sought in the manner used by Richards and Forbes in the case of silver nitrate, are needed to settle the third decimal place in the atomic weights of silver and chlorine beyond doubt, but the present investigation seems unquestionably to show that the atomic weights proposed by Stas, both for silver and for lithium, were much too high, and that the recent conclusion of many chemists that the value for silver is not far from 107.88 is entirely justified.

It is worthy of note that this investigation, taken together with that of Richards and Wells, gives values for chlorine, lithium and silver referred to oxygen which are independent of all other work. That these values should agree so closely with other results obtained in such widely different ways is very reassuring as to the degree of precision now within reach.

Summary.

This investigation consisted in a careful study of three ratios, namely that of lithium chloride to silver chloride, that of lithium chloride to silver, and that of lithium chloride to lithium perchlorate. By means of the last two ratios, O_4 : Ag was calculated, and new values were obtained in this entirely new way for the atomic weights of silver, lithium and chlorine. In the process of this work new methods of purifying lithium salts, better than any preceding, were devised. Lithium chloride was fused in such a way as to show perfect neutrality to the most sensitive indicators, and was weighed in a strictly anhydrous condition. The preparation of perchloric acid also was subjected to rigid scrutiny, and this substance was made in a state of unusual purity. The sharpness of the end-point in the method used for determining the relation between silver and chlorine was much increased by cooling the solution to 0°, in order to diminish the solubility of silver chloride. In other respects the methods of analysis developed in previous Harvard investigations were used in the determination of chlorine. A new precise method was devised for converting lithium chloride into lithium perchlorate, and its sources of error were carefully examined. 45.56877 grams of lithium chloride were found in seven experiments to yield 154.0602 grams of silver chloride on complete precipitation; and in another series of seven experiments partly independent from these 46.63197 grams of lithium chloride were found to need 118.65894 grams of silver for complete precipitation. In yet another series of six experiments, entirely independent, but using a similar preparation of lithium chloride, 34.40566 grams of this substance were converted into 86.34716 grams of lithium perchlorate. As an outcome of all these experiments, the atomic weight of lithium was found to be 6.939, and the atomic weight of silver 107.871, if oxygen is taken as 16.000.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. No. 45.]

THE SOLUBILITY OF SILVER CHLORIDE, BARIUM SULPHATE, AND CALCIUM SULPHATE AT HIGH TEMPERATURES.

BY ARTHUR C. MELCHER.

Received November 1, 1909.

Contents.

1. Outline of the investigation. 2. Previous investigations upon these substances. 3. Apparatus and method. 4. Preparation of the materials. 5. Conductance of solutions saturated with silver chloride and barium sulphate. 6. The solubility values for silver chloride and barium sulphate. 7. Conductance of calcium sulphate solutions of known concentration. 8. The specific conductance of solutions saturated with calcium sulphate. 9. The solubility values for calcium sulphate. 10. Discussion of the solubility relations of calcium sulphate. 11. Summary.

1. Outline of the Investigation.

The solubility of many difficultly soluble salts at room temperatures has already been determined by several investigators[1] by means of measurements of the electrical conductance of the saturated solutions. At the higher temperature of 100° Böttger,[2] working in this laboratory with the platinum-lined steel bomb used for conductivity measurements, determined the conductance of the saturated solutions of three silver salts.

The purpose of the present investigation was to apply this method to other salts at the high temperatures. The solubilities of silver chloride and barium sulphate, which are of great importance in analytical chemistry, were determined at 18, 50 and 100°. In addition, conductance measurements of saturated solutions of calcium sulphate were made at the temperatures 18, 50, 100, 156 and 218°, and the solubility and existence of its three forms, gypsum, soluble anhydrite, and ordinary anhydrite, were studied by this method. This substance was chosen for investigation partly because of the great importance of a knowledge of its solubility relations from the standpoint of geological and industrial chemical processes.

2. Previous Investigations upon These Substances.

Kohlrausch and Rose, Holleman, and Böttger[3] measured the conductance of saturated solutions of silver chloride, barium sulphate, and gypsum at temperatures between 2 and 42°. After subtracting the measured conductance of the water, they calculated the corresponding solubility by means of approximate values of the equivalent conductance at zero concentration. Two later articles of Kohlrausch give new values of the solubility, based upon more recent determinations of the equivalent conductances.

---

[1] F. Kohlrausch and Rose, *Z. physik. Chem.*, 12, 234 (1893); Holleman, *Ibid.*, 12, 125 (1893); F. Kohlrausch, *Ibid*, 44, 197 (1903); 64, 129 (1908); W. Böttger, *Ibid.*, 46, 521 (1903).

[2] *Z. physik. Chem.*, 56, 83 (1906).

[3] *Loc. cit.*

Goodwin[1] calculated the solubility of silver chloride at 25° from measurements of the potential difference of two silver electrodes, one of which was placed in a silver nitrate solution and the other in a potassium chloride solution saturated with silver chloride.

Böttger, as above stated, made preliminary experiments on the solubility of silver chloride at 100° in the platinum-lined bomb.

The solubility of gypsum between 0 and 100° has been determined by numerous investigators by evaporating a known volume of its saturated solution and weighing the residue. The literature relating thereto has been discussed by Hulett and Allen[2] in connection with their own careful determinations.

At higher temperatures Tilden and Shenstone[3] made rough measurements by heating an excess of solid salt with water in a silver-plated gun-metal tube, decanting while still hot through a platinum gauze partition into another part of the tube, cooling in the air, and analyzing the decanted solution. Boyer-Guillon[4] determined the solubility of calcium sulphate by heating a solution of it in a bronze autoclave for some hours at the temperature in question and then withdrawing portions through an asbestos filter.

3. Apparatus and Method.

The conductance measurements were made in a bomb such as is described by Noyes and Coolidge.[5] The electrode was of platinum-iridium, a cylinder dome-capped in shape, and polished so that none of the solid salt in suspension would adhere to it. The bomb carriage[6] was connected by means of gearing to an electric motor so that the bomb could be turned over and over continuously about twelve times per minute. The measurements from 18–156° were made in this way within an electrically heated bath of liquid pseudocumene. Those at 218° were made in a naphthalene-vapor bath, the bomb being rotated occasionally by hand.

The conductance capacity of the bomb was determined by measuring in it the conductances of 0.002 normal potassium and sodium chloride solutions at 18°, and was thus found to be 0.1224 and 0.1225.

It was proved that the conductance of a 0.01 normal potassium chloride solution in the bomb was not measurably changed by the addition of some solid silver chloride, showing that the presence of the solid in suspension would make no appreciable error in the conductance measurements.

---

[1] *Z. physik. Chem.*, **13**, 645 (1894).

[2] This Journal, **24**, 676–9 (1902).

[3] *Phil. Trans. Royal Soc.*, **175** *A*, 31 (1884).

[4] *Ann. Conservatoire Arts et Metiers* [3], **2**, 207 (1900).

[5] *Publ. Carnegie Inst., Washington*, **63**, 59.

[6] *Loc. cit.*, p. 64.

The solubility determinations were made in the following manner, except in the cases noted in a later section: About one cubic centimeter of the moist well-washed salt was placed in the bomb and further washed by decantation. Water whose conductance had been determined in a glass cell was introduced into the bomb, and the bomb was closed. The bomb was next rotated at each successive temperature until the conductance was constant for fifteen minutes. The bomb was then carefully opened and the solution decanted off, a quantity of fresh water was added to the same salt, and the process was repeated until the conductances of the successive solutions at each temperature were practically identical.

Conductance measurements with water alone were made in the bomb under the same conditions, so as to determine the water correction. In these cases, the same method of treatment and the same time of heating were followed. The results are given in Table I:

Table I—Values of the Specific Conductance × 10^6 of Water.

Date 1908.	Glass cell (18°).	Bomb at 18°.		Bomb at 50°		Bomb at 100°.
		Initial.	Final	Initial	Final.	
Feb. 5	. . 0.49	0.65	0.68	1.29	1.34	2.66
Feb. 7.	. . . . 0 47	0.58	0.67	1 15	1.24	2.25
Feb. 11	. . . . . . 0.55	0.72	0.79	1.28	1.42	2.42
Mean,	0.50	0.65	0.71	..24	1.34	2.45

4. Preparation of the Materials.

Two samples of silver chloride were prepared in a photographic darkroom illuminated only by red light. Sample I was prepared as follows: A solution, approximately 0.1 normal, of silver nitrate was heated to 100° in a water bath. A solution of 0.1 normal hydrochloric acid was dropped slowly into the hot silver nitrate solution with constant stirring. The silver chloride was washed by decantation, the chloride settling out very quickly. Sample II was prepared in the same way from silver nitrate and potassium chloride solutions. The washed chloride was, however, in this case further washed by shaking with a dilute ammonia solution in a bottle. The remaining chloride was treated with cold ammonia, 0.96, until about three-fourths of it had dissolved, and the solution was separated by decantation. This solution was heated slowly with vigorous stirring, and the precipitated chloride was washed by decantation. Both samples were kept under water in the dark.

Barium sulphate was prepared by dropping a 0 1 normal barium chloride solution into a hot 0.1 normal sulphuric acid solution which was constantly agitated by a revolving stirrer. The salt was washed by decantation and rotated for hours in hot water. The smaller particles were then washed away by decantation.

Calcium sulphate was prepared both in the form of gypsum and of anhydrite. A quantity of Kahlbaum's C. P. calcium sulphate was washed by long agitation with several portions of water. Conductivity water was then saturated with this salt at the temperature of its maximum solubility (35–40°), and the solution was then partially evaporated at a temperature below 60°, yielding the sample of gypsum. The anhydrite was obtained by dehydrating the salt so obtained by heating at 200° for twelve hours, when a constant weight had resulted.

The water used in the solubility determinations was prepared by redistilling ordinary distilled water to which alkaline permanganate solution was added, from a copper still with a tin condenser. This water was used directly in the work with calcium sulphate. For the solubility experiments with silver chloride and barium sulphate, this water was again redistilled from a special tin-lined still with a block-tin condenser. Only those portions from either distillation which had a specific conductance less than 0.8×10^{-6} were used in the investigation.

5. Conductance of Solutions Saturated with Silver Chloride and Barium Sulphate.

The specific conductances of the saturated solutions of silver chloride and barium sulphate are given in Table II. The column headings are for the most part self-explanatory. All the conductance values are expressed in reciprocal ohms and multiplied by 10^6. The specific conductance value given for the water employed are those measured in the glass cell at 18 or 25°:

TABLE II.—SPECIFIC CONDUCTANCE DATA FOR SATURATED SOLUTIONS OF SILVER CHLORIDE AND BARIUM SULPHATE.

Date. 1908.	Salt and sample. AgCl.	Water at 18 or 25°.	18 or 25°.[1]		50°.		100°.		
			Init.	Fin.	Init.	Fin.	Init	Fin.	156°.
Feb. 19	I	0.61	2.08	2.94	9.39	10.75	61.8	....	....
Feb. 20	..	0.54	2.06	3.04	9.46	10.75	61.6	....	...
Feb. 26	...	0.54	2.05	2.91	9.32	10.60	61.6	....	....
Feb. 27	.	0.49	1.89	2.48	9.10	9.96	61.2	....	....
Feb. 28	II	0.49	2.00	3.52	9.75	11.78	63.3	...	....
Mar. 2		0.65	1.99	2.73	9.25	10.40	62.0	...	....
Mar. 3		0.56	2.00	2.52	9.32	10.03	61.6	....	...
	BaSO$_4$.								
July 27	I	0.80	3.90[2]	8.82	7.85	...	16.93	....	24.1
July 28		0.60	3.75[2]	6.42	7.79	11.60	16.54	21.2	20.2[3]
July 29		0.65	3.81	3.99	7.73	7.93	16.45	....	....
			(3.99)	6.60	....	...	...	....	19.8[4]

[1] 18° in the experiments with AgCl, 25° in those with BaSO$_4$.

[2] The values at 18° were 3.01 and 2.94 in these two experiments.

[3] This increased to 24.6 in 45 minutes.

[4] This increased to 25.0 in 30 minutes.

The conductance of the saturated silver chloride solutions became constant in about twenty minutes. Preliminary experiments carried to the higher temperature 156° showed the impracticability of making any determinations above 100°. The large increase of conductance with the time in the case of barium sulphate at 156° is shown in the footnotes of the table. When, as in the third experiment, the solution was not heated above 100°, the final value at 25° is seen to be only slightly larger than the initial value; but when heated to 156°, as in the first two experiments, it was nearly doubled in less than an hour. The last row in the table shows directly the effect of heating to 156° the solution (represented by the row above) which had been previously heated to 100°.

6. The Solubility Values for Silver Chloride and Barium Sulphate.

From the specific conductances of the saturated solutions given in Table II, the conductance of the water was first subtracted, this being derived from Table I by multiplying the mean "bomb" values there given by the ratio to 0.50 of the specific conductance shown by the water in question when measured in the glass cell. As final values for barium sulphate were adopted the so-called initial values obtained in the last experiment (on July 29th) when the salt had been most fully leached out. As final values for silver chloride at 18 and 50° the mean of the initial values obtained in the last experiment with each sample (on Feb. 27th and March 3rd) were adopted. The value for silver chloride at 100° was corrected by determining the temperature coefficient of the contamination from the difference of the initial and final values at 18 and 50° and subtracting the proportionate value at 100°. The following specific conductances × 10^6 were thus derived:

TABLE III.—SPECIFIC CONDUCTANCE OF SATURATED SOLUTIONS OF SILVER CHLORIDE AND BARIUM SULPHATE.

Substance.	18°.	25°.	50°.	100°.
Silver chloride........	1.26	....	7.90	57.9
Barium sulphate........	2.30	3.00	6.45	14.0

By dividing the values given in Table III by the sum of the equivalent conductances of the separate ions, as given by Johnston,[1] the ion-concentrations in the saturated solutions were calculated. The results expressed in milli-equivalents per liter are given in Table IV:

TABLE IV.—ION CONCENTRATION IN THE SATURATED SOLUTIONS OF SILVER CHLORIDE AND BARIUM SULPHATE.

Substance.	18°	25°.	50°.	100°.
Silver chloride.............	0.0105	....	0.0363	0.146
Barium sulphate............	0.0187	0.0208	0.0281	0.0322

---

[1] THIS JOURNAL, 31, 1015 (1909). The values of Λ_0 which were employed are

	18°.	25°.	50°.	100°.
AgCl..................	119.8	...	217	395
$BaSO_4$..................	123	144	229	434

These values of the ion-concentration differ somewhat from those of the total concentration of the salt in the saturated solutions. The extent of the difference may be determined by estimating the degree of ionization in these very dilute saturated solutions by means of the ionization formula $(1 - \gamma) = K\,C^{0.5}$, which corresponds to the conductance formula employed by Kohlrausch. The constant K for barium sulphate was assumed to be the same as for calcium and magnesium sulphates, and was derived for these salts from the ionization data at 2 millinormal given in Table VIII. That for silver chloride was assumed to be the same as for silver nitrate, the ionization value for the latter at 2 millinormal given by Noyes and Melcher being employed. By dividing the ion concentration given in Table IV by the ionization values so determined, the total concentrations (in milli-equivalents per liter) in the saturated solutions, given in Table V, were obtained:

TABLE V.—SOLUBILITY OF SILVER CHLORIDE AND BARIUM SULPHATE.

Substance.	18°.	25°.	50°.	100°.
Silver chloride	0.0105	...	0.0365	0.147
Barium sulphate	0.0190	0.0212	0.0288	0.0334

These results at 18° may be compared with those previously found by Kohlrausch and Böttger. Kohlrausch's[1] values are 0.0094 for silver chloride and 0.0197 for precipitated barium sulphate. It seems probable that the lower values are more accurate in each case. Böttger's[2] values for silver chloride at 19.95° were 3 per cent. larger than Kohlrausch's. His value[3] for the specific conductance of that salt at 100° is 56.7×10^{-6}, which is nearly identical with that given in Table III. When divided with the same Λ_0 value as that used by me, it gives a solubility of 0.0143 milli-equivalents per liter. At the time of his measurements the agitation of the bomb was done by hand instead of by a mechanical rotating arrangement, which made the securing of saturation at exactly 100° more difficult.

From the solubilities of these salts at 18, 50, and 100°, the heat absorbed by the solution of one formula weight of the salt was calculated by solving the two simultaneous equations:

$$\log_e \frac{S_{50}}{S_{18}} = \frac{L_0}{2R}\left(\frac{1}{291} - \frac{1}{323}\right) + \frac{\alpha}{2R}\log_e \frac{323}{291}.$$

$$\log_e \frac{S_{100}}{S_{50}} = \frac{L_0}{2R}\left(\frac{1}{323} - \frac{1}{373}\right) + \frac{\alpha}{2R}\log_e \frac{373}{323}.$$

These are the forms obtained by integrating the fundamental thermodynamic equation

---

[1] *Z. physik. Chem.*, 64, 148, 152 (1908).

[2] *Ibid.*, 46, 602 (1903).

[3] *Ibid.*, 56, 93 (1906).

$$d \log S = \frac{L}{2RT^2}\, dT$$

for the case that $L = L_0 + \alpha T$, and by substituting the appropriate values of T.

By these calculations the value in calories of L, the heat absorbed by the solution of one formula weight of the salt at the absolute temperature T was found to be:

$$L = 34200 - 60.5\ T \text{ for silver chloride;}$$

and $$L = 30800 - 85.2\ T \text{ for barium sulphate.}$$

For $T = 273 + 18$, this expression yields:

$$L = 16600 \text{ cal. for AgCl; and } L = 6000 \text{ cal. for } BaSO_4.$$

The heat evolved by the precipitation of these salts when produced by the metathesis of silver nitrate and hydrochloric acid or of soluble barium salts and sodium sulphate was found by Thomsen to be 15800 calories for silver chloride[1] and to be 4970 calories for barium sulphate.[2] Considering the inaccuracy of the very small solubility values at 18°, the agreement is perhaps as close as could have been expected.

7. Conductance of Calcium Sulphate Solutions of Known Concentration.

A stock solution of calcium sulphate was made by dissolving some of the salt in conductivity water. The concentration was determined by precipitating the calcium as oxalate, filtering, and washing the precipitated calcium oxalate, and then titrating it in hot acid solution with potassium permanganate solution, which had been standardized against sodium oxalate ("nach Sörensen") It contained 23.50 milli-equivalents per liter. More dilute solutions were made by weighing out some of the stock solution and making up to a known volume.

The conductivity data are given in Table VI. The first two columns are self-explanatory. The third column gives the concentration at the temperature of the measurement expressed in milli-equivalents per liter. The fourth column gives the specific conductance of the solution corrected for all instrumental errors. The fifth column gives the calculated equivalent conductance after correcting for the conductance of the water.

Using as a means of interpolation the formula $C(\Lambda_0 - \Lambda) = K(C\Lambda)^{1.5}$, the values at round concentrations given in Table VII were obtained. The values at zero concentration are the sums of those derived for the calcium and sulphate ions by Johnston[3] from measurements with other substances.

---

[1] Ostwald's *Lehrbuch d. allgemeinen Chem.*, 2, I, 335.

[2] Thomsen's "Thermochemistry," Ramsay's Series, p. 118. Mean of the results with barium chloride, nitrate, and chlorate.

[3] THIS JOURNAL, 31, 1015 (1909)

TABLE VI CONDUCTANCE OF CALCIUM SULPHATE SOLUTIONS

Date. 1908	Concentration at 4°.	Temperature t°	Concentration at t°.	Specific conductance x 10^6.	Equivalent conductance.
May 11. .	1.976[1]	18	1.973	193.7	97.8
		50	1.952	346.7	176.7
		100	1.894	568.0	299.0
		156	1.799	637.0	352.0
May 5	3.951	18	3.946	354.7	89.7
		50	3.904	629.0	160.8
		100	3.788	990.0	261.0
		156	3.598	1044.0	289.0
		18	3.946	355.1	89.8
May 6	7.988	18	7.978	645.0	80.7
		50	7.894	1127.0	142.7
		100	7.658	1706.0	222.0
May 7	23.53	18	23.50	1558.0	66.2
		50	23.25	2640.0	113.5
		100	22.55	3800.0	168.5

The value of the exponent n in the expression $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$ that best corresponds to these results at 18° was found to be 1.50. It is therefore of about the same magnitude as in the case of the uni-univalent and uni-bivalent salts previously studied. In the case of the values of Hulett, which extend over a wider range of concentration, the double curvature[2] due to a change in the value of the exponent n was clearly evident.

TABLE VII.—EQUIVALENT CONDUCTANCE OF CALCIUM SULPHATE AT ROUND CONCENTRATIONS.

Concentration	18°.	50°.	100°.	156°.
0	119.0	223.0	425.0	682
2.0	97.7	176.0	295.0	341
4.0	89.6	160.0	258.0	280
8.0	80.7	142.4	220.5	
10.0	77.7	136.5	209.0	
20.0	68.5	118.0	174.0	

Plotting the data of Hulett[3] in the same way, so as to get the values of the equivalent conductance for corresponding concentrations, the following results were obtained. The two series are seen to be in excellent agreement:

Concentration.	Melcher.	Hulett.
2.00	97.7	97.4
4.00	89.6	89.6
8.00	80.7	80.7
10.00	77.7	77.7
20.00	68.5	68.6

---

[1] This soluti[illegible] was heated to 218°, but even this dilute solution was so supersaturated th[illegible] it began to precipitate out before the temperature was reached.

[2] [illegible] value [illegible] AL, 31, 74[illegible]

From the equivalent conductance values given in Table VII, the ratio $100\ \Lambda/\Lambda_0$ corresponding to the percentage ionization of the calcium sulphate was calculated. The resulting values are given in Table VIII beside those previously obtained[1] for magnesium sulphate. The degree of ionization of calcium sulphate is seen to be substantially the same as that of magnesium sulphate at 18°, but distinctly less at 100 and 156°.

TABLE VIII.—PERCENTAGE IONIZATION OF CALCIUM SULPHATE.

Temperature.	Concentration.	$CaSO_4$.	$MgSO_4$.
18°............	2	82.0	82.6
	10	65.2	66.7
	20	57.5	59.2
50°...	2	79.0	...
	10	61.0	..
	20	53.0	....
100°............	2	69.0	71.0
	10	49.0	52.0
	20	41.0	45.0
156°...............	2	50.0	55.0

8. The Specific Conductance of Solutions Saturated with Calcium Sulphate.

The data obtained with the saturated solutions of calcium sulphate are contained in Table IX. The first column contains the number of the experiment, each series of measurements made with a new charging of the bomb with fresh water being indicated by a letter attached to the preceding number and each series where both salt and water were renewed being given a separate number. The second column contains the date. The third shows the form of solid salt which had been originally introduced, G representing gypsum and A anhydrite. The fourth column contains the (corrected) temperature. The fifth and sixth columns show the values of the specific conductance in reciprocal ohms multiplied by 10^6, those under "first value" being measured as soon as the temperature of the bath had presumably been attained and those under "last value" being measured after the interval of time in minutes shown in the seventh column. The last column shows the change in specific conductance per minute which was still taking place during the last ten minutes of that interval; where dots are inserted, the reading was constant. Whether saturation was approached from a higher or lower temperature is indicated by the temperature given in the row next above, except that in passing from 218 to 156° the bomb was always cooled *below* the latter temperature before introducing it into the bath.

---

[1] *Publ. Carnegie Inst., Washington* date.

TABLE IX.—CONDUCTANCE DATA FOR THE SATURATED SOLUTIONS OF CALCIUM SULPHATE.

Expt. No.	Date. 1908.	Substance added.	Temperature.	Specific conductance × 10⁶		Time interval.	Change per minute.
				First value.	Last value.		
1	Mar. 26	G	18	1785	1860	60	.
			50	3200	3225	35	.
	Mar. 27		100	3940	3880	40	. .
			156	1605	1600	30	
			218	460	375	50	—3 1
	Mar. 30		18	1820	1920	30	+3.0
2	Mar. 30	G	18	1805	1865	60	..
			50	3220	3225	30	....
	Mar. 31		100	3890	3885	20	. ..
			156	1600	1580	30	.
3	Apr. 2	G	18	1860	1870	30	
			50	3230	3230	25	. .
			100	3925	3880	30	
			156	1600	1590	30	.
	Apr 3		218	463	290	120	
	Apr. 6		156	1600	1040	400	—0.25
	Apr. 7		218	358	315	60	.
4	Apr. 9[1]	A	100	4210	4045	50	
			156	1545	955	220	—0.25
			218	225	235	140	.
			156	930	870	75	..
			100	1950	2035	75	+0.4
4*a*	Apr. 13		100	2970	2690	60	—1.4
			156	1200	915	60	—1.0
			218	230	210	60	
			156	935	835	40	
			161[2]	.. .	(755)	.	
			156	810	830	30	.
			100	1860	1975	30	..
			95[2]	....	(2055)	.	...
			100	2050	2030	30	—0.4
4*b*	Apr. 14		218	232	202	70	.. .
			161[2]	....	(795)	..	
			156	795	840	45	.
			100	1845	1965	30	. .
			95[2]	.	(2020)	.	..
			100	2015	1990	45	—0.2
5	May 21	G	50	3230	3225	30	.. .
5*a*	May 21		18	1865	1870	20	. ..
			50	3230	3225	20	.
			100	3880	3880	20	. ..

[1] From April 9th to 14th, inclusive, the substance was always in contact with a solution whose temperature was above the transition point of gypsum and anhydrite.

[2] The bomb was rotated in the neighborhood of these temperatures until the conductance was practically constant. The values of the latter (enclosed within parenthesis) are very rough ones.

TABLE IX.—CONDUCTANCE DATA FOR THE SATURATED SOLUTIONS OF CALCIUM SULPHATE—(*Continued*).

Expt. No.	Date. 1908.	Substance added.	Temperature.	Specific conductance × 10^6 First value.	Specific conductance × 10^6 Last value.	Time interval.	Change per minute.
			110[1]		(3750)		.
			100	3870	3885	20	..
			135[1]	.	(2510)		...
			100	3820	3825	25	....
			156	1625	1560	30	....
			100	3810	3825	15	....
			50	5250	5850	40	+1.1
	May 22		100	4520	3830	85	...
			67[1]	...	(3675)		..
			100	4135	3825	70	....
			50	3275	3185	30	....
	May 25		156	1565	1560	240	....
			100	3825	3825	60	.
			50	.	5660	90	+1.1
	May 26		50		3225	180	
	May 27		218		216	450	
	May 28		218	222	215	90	
			156	820	830	60	
			100	1740	1950	110	..
			50	2300	2635	35	+3.0

In deriving final values of the conductance and solubility at the different temperatures it is necessary to take into consideration the character of the solid phase in contact with the solution, for this may be present in different forms under the different conditions. To make clear the relations here involved, the results of two of the most complete experiments (No. 5*a* and the latter part of No 4*a*) are represented graphically in Figure 1, in which the abscissae denote somewhat arbitrary intervals of time. The upper graph shows the behavior of a solution made by introducing gypsum as the solid substance. This is the solid phase still present in the first measurement at 100°, and the figure shows that heating to 110° for a short time does not transform it, since on returning to 100° the conductance has the same value as before. After heating to 135°, however, the conductance is seen to return to an appreciably lower value at 100°, and this same value is again obtained after heating to 156°. Considering now the lower graph, which represents the behavior of a solution made by adding anhydrite to hot water (above 70°), it will be seen that upon coming down from 218 to 156° and later to 100° much lower values of the conductance are obtained at both temperatures

---

[1] The bomb was rotated in the neighborhood of these temperatures until the conductance was practically constant. The values of the latter (enclosed within parenthesis) are very rough ones.

(whether approached from above or a little below) than in the other experiment where gypsum was the added substance. These facts make

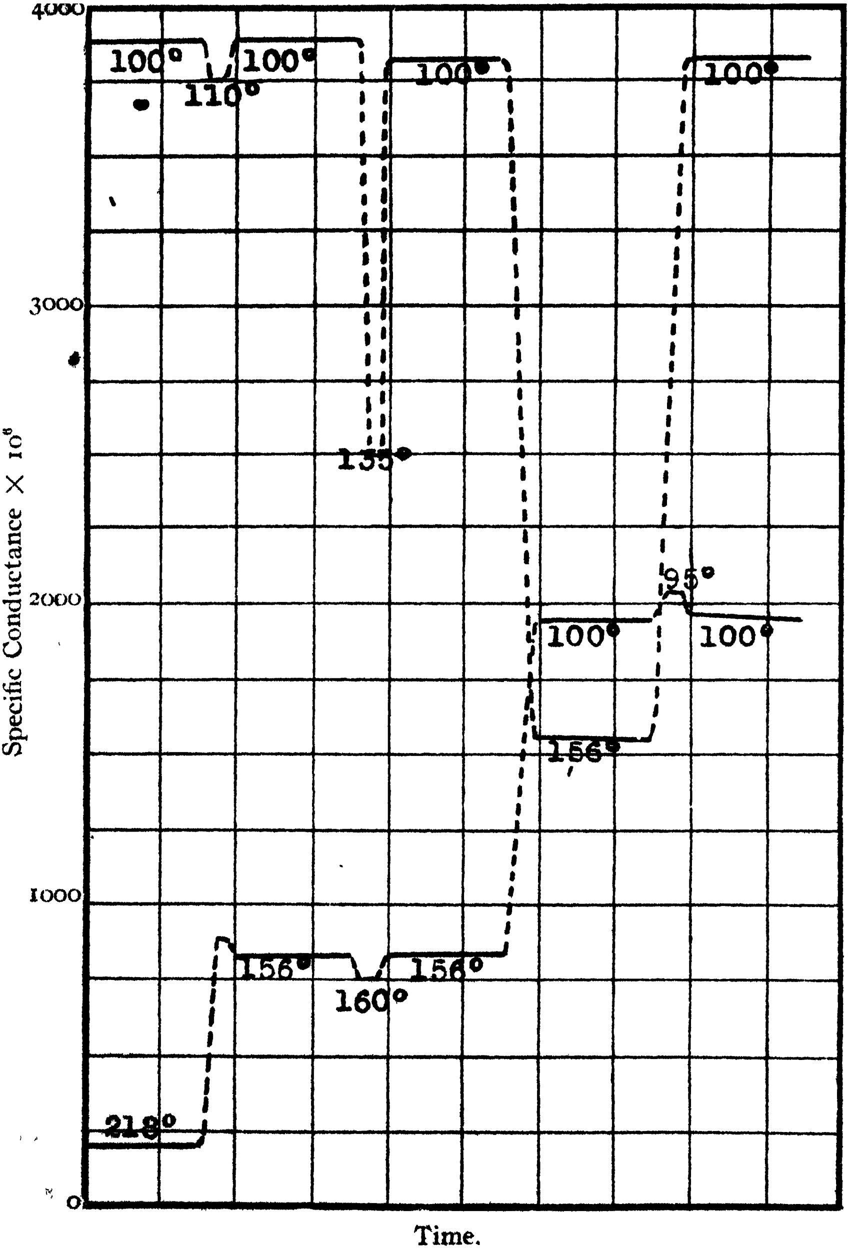


Fig. 1.

it clear that there are in the different cases three different solid phases involved. That corresponding to the highest conductance value at 100° is doubtless gypsum, and that corresponding to the lowest conductance values at 100° and at 156° is doubtless ordinary anhydrite. The intermediate value at 100° and the higher one at 156° must correspond to a third solid phase. This might be either another hydrate or another form of the anhydrous salt. Its solubility relations, namely, the temperature at which its solubility curve intersects that of gypsum and the constancy (at 100 and 156°) of the ratio of its solubility to that of the anhydrite, prove, as will be seen below, that it is the latter and that it is undoubtedly identical with the "soluble anhydrite" of van't Hoff.[1]

Table X contains final values of the conductance of the solutions saturated with these three different forms:[2]

TABLE X.—SPECIFIC CONDUCTANCE × 10^6 OF THE SATURATED SOLUTIONS OF CALCIUM SULPHATE.

	18°.	50°.	100°.	156°.	218°.
Gypsum	1867	3226	3882	....	..
Soluble anhydrite	....	....	3825	1560	..
Anhydrite	....	....	1963	834	211

9. The Solubility Values for Calcium Sulphate.

To determine the corresponding solubility values, the concentrations of calcium sulphate, which would give at the various temperatures the specific conductances recorded in Table X, were calculated as follows: With the data given in Table V for solutions of known concentration plots of $1/\Lambda$ against $(C\Lambda)^{0.5}$ were made, Λ representing as usual the equivalent conductance, C the equivalent concentration, and $C\Lambda$ therefore the specific conductance × 10^8. From these plots the values of Λ corresponding to the values of the specific conductance of the saturated solution were taken off, and by dividing the latter by the former values, the concentrations of the saturated solutions were obtained. The result at 218°, however, is only an estimate obtained by dividing the fairly accurate value of the ion concentration in the saturated solution given below in Table XIII, by the degree of ionization, this latter being estimated to be about 30 per cent. through a consideration of the ionization values at 218° obtained for magnesium sulphate by Noyes and Melcher.[3]

---

[1] *Z. phys. Chem.*, 45, 273 (1903).

[2] For the solutions saturated with gypsum at the various temperatures these values are means of all the "last values." For the solutions saturated with anhydrite the mean of the last four values at 156 and 218° given in the table was taken, and at 100° for both forms of anhydrite the mean of all the constant values was taken. For the soluble anhydrite at 156° the mean of the last two measurements was taken.

[3] By plotting their values of the ionization γ against $(C\gamma)^{0.5}$ and extrapolating, it is found that $\gamma = 0.36$ for $C\gamma = 0.2$ millinormal; and we have assumed that for calcium sulphate the value is 15 per cent. less than this, upon the basis of the results at 156°.

This solubility value at 218° is almost certainly correct within 0.1 milli-equivalent.

Table XI contains the solubility values expressed in milli-equivalents per liter:

TABLE XI.—SOLUBILITY VALUES FOR CALCIUM SULPHATE.

Form.	18°.	50°.	100°.	156°.	218°.
Gypsum	29.5	30.0	23.3	...	...
Soluble anhydrite	. .	....	22.8	6.4	...
Anhydrite	....	....	9.2	2.7	0.7

The results obtained by other investigators or interpolated from their values are placed beside mine in Table XII:

TABLE XII.—COMPARISON OF THE SOLUBILITY VALUES WITH THOSE OBTAINED BY OTHER INVESTIGATORS.

Solid phase	Temperature.	Melcher.	Hulett and Allen.[1]	Boyer-Guillon.[2]	Tilden and Shenstone.[3]
Gypsum	18°	29.5	29.6	...	...
"	50°	30.0	30.1	...	...
"	100°	23.3	23.8	24.2	...
Anhydrite	200°	0.9	...	....	...
Soluble anhydrite	200°	. .	. .	2.3	3.7

It will be seen that the new values agree almost perfectly with those obtained by Hulett and Allen by an entirely different method. They also agree well with the results of Boyer-Guillon at 100 and 156°. His much higher value at 200° seems clearly to have been due to the fact that the solid phase in contact with the solution was still soluble anhydrite. This conclusion is confirmed by the fact that the ratio (2.3 : 0.9 = 2.5) of the solubility of the two anhydrites at 200° is nearly the same as that (2.4) at 156°—a relationship discussed more fully below. His results therefore supplement those here presented in an important way by showing the solubility of that phase at higher temperatures than those at which it was determined in these experiments. The values of Tilden and Shenstone are probably too high, owing to errors involved in their method.

It seems desirable to give also the values of the equivalent concentrations of the ions in the saturated solutions. These are given in Table XIII. They were obtained by dividing the measured values of the specific conductance given in Table X by the values of $\Lambda_{Ca} + \Lambda_{SO_4}$ (at zero concentration) as computed by Johnston:[4]

---

[1] THIS JOURNAL, 24, 474 (1902).

[2] *Ann. Conservatoire Arts et Metiers* [3], 2, 209 (1900).

[3] *Trans. Roy. Soc.* (*London*), 175*A*, 31 (1884).

[4] THIS JOURNAL, 31, 1015 (1909). The values of $\Lambda_{Ca} + \Lambda_{SO_4}$ employed are:

18°.	50°.	100°.	156°.	218°.
119	223	4.25	68.2	1060

The value at 218°, not being given by Johnston, was assumed to be somewhat (2 per cent.) less (as at 156°) than that previously computed for magnesium sulphate by Noyes and Melcher.

TABLE XIII.—EQUIVALENT CONCENTRATION OF IONIZED CALCIUM SULPHATE IN THE SATURATED SOLUTIONS.

Form.	18°.	50°.	100°.	156°.	218°.
Gypsum	15.69	14.47	9.13	. . .	. . . .
Soluble anhydrite			9.00	2.29	. . . .
Anhydrite			4.62	1.22	0.20

A comparison of these values with those given in Table XI shows that the ionization in the solution saturated at 100° with gypsum is 39 per cent. and that that in the solution saturated at 156° with anhydrite is 45 per cent.

10. Discussion of the Solubility Relations of Calcium Sulphate.

In order to make clearer the solubility relations of calcium sulphate, the values given in Table XI are represented graphically in Fig. 2. The curve given for gypsum has been completed with the aid of the data of Hulett and Allen, and that for soluble anhydrite with the aid of those of Boyer-Guillon. An additional point at 60° upon the anhydrite curve has been furnished by van't Hoff's determination[1] of the transition temperature for gypsum and anhydrite.

Attention may be called to the following facts shown by a consideration of the diagram and the values of Table XI:

Anhydrite is the stable form at temperatures above 60°. Its solubility decreases with great rapidity with rising temperature, having at 218° a value only one-fortieth as great as that of gypsum at 18°.

The solubility curve for soluble anhydrite cuts that for gypsum at a point corresponding to a temperature of about 97°. The transition temperature of these two forms was estimated by van't Hoff[2] from vapor-pressure measurements to be 93°, thus a few degrees lower. The agreement is, however, as close as could be expected.

The ratio of the solubility of soluble anhydrite to that of ordinary anhydrite is almost the same at 100 and at 156°, namely 2.48 at 100° and 2.37 at 156°. This fact is significant in showing that the former solid substance is, as assumed, another form of anhydrous calcium sulphate and not a hydrate, for it follows from the thermodynamic equation $d \log \frac{S_{II}}{S_{I}} = \frac{Q}{RT^2}\, dT$, that, when S_{II}/S_{I}, the ratio of the solubilities of the two forms is constant, the heat of transition Q is zero. While this would be highly improbable for the transition of an anhydrous into a hydrated salt, it is to be expected that the value of the heat of transition of two solid anhydrous substances of the same chemical composition would be very small.

---

[1] See Landolt-Bornstein-Meyerhoffer Tabellen, p. 529.

[2] *Z. phys. Chem.*, **45**, 279 (1903). Compare, however, the statements of Davis (*J. Soc. Chem. Ind.*, **26**, 732 (1907)) in regard to this equilibrium.

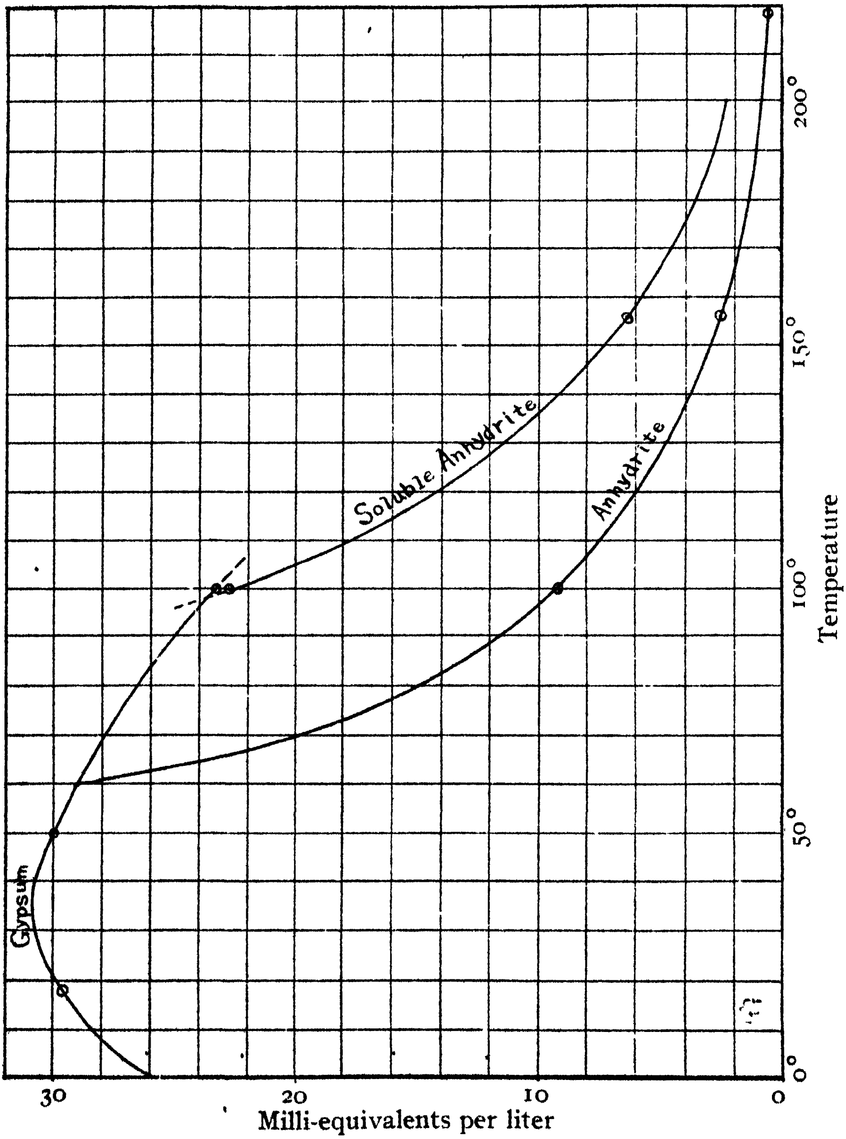


Fig. 2.

11. Summary.

In this article have been presented the results obtained by measuring in a platinum-lined steel bomb provided with a mechanism for rotating it within a liquid bath the conductance of solutions saturated separately with silver chloride and barium sulphate at 18, 50, and 100°, and with calcium sulphate at these temperatures, and also at 156 and 218°. The corresponding solubilities were calculated by dividing the values of the specific conductance so obtained by the appropriate values of the equivalent conductance, which last were derived in the case of the first two salts from the values for the separate ions at zero concentration, and in the case of the calcium sulphate from measurements (also presented above) of the conductance of solutions of it of known concentration. The final solubility values will be found in Tables V and XI, on pages 55 and 63. The heats of solution of silver chloride and barium sulphate were also calculated from these data.

In the case of calcium sulphate, the investigation included the study of the solubility relations of the three forms: gypsum, soluble anhydrite, and ordinary anhydrite. These relations are represented graphically in Fig. 2 on page 65. The transition temperature for the metastable system gypsum, soluble anhydrite, solution, was found, from the point of intersection of the solubility curves, to be about 97°. The solubility of the ordinary anhydrite was shown to decrease enormously with rising temperature, namely from 29.0 milli-equivalents per liter at 60°, where, according to van't Hoff, it is in stable equilibrium with gypsum, to 0.7 milli-equivalents per liter at 218°.

The ion concentrations in the saturated solutions of calcium sulphate have also been calculated and presented in Table XIII, on page 64.

The ionization relations of calcium sulphate have been compared with those for magnesium sulphate previously investigated in this laboratory by Noyes and Melcher. At 18° the degrees of ionization of the two salts are nearly identical; but at 100 and 156° the ionization of the calcium salt is a few per cent. less than that of the magnesium salt at corresponding concentrations.

This investigation has been carried out under the direction of Professor A. A. Noyes with the aid of a grant made to him by the Carnegie Institution of Washington. It is desired to express here grateful acknowledgment of this financial aid, by which this research has been made possible.

BOSTON, October. 1909.

THE PREPARATION OF PERCHLORIC ACID FROM SODIUM PERCHLORATE.[1]

BY FRANK C. MATHERS.

Received October 11, 1909.

Most of the methods for the preparation of perchloric acid depend upon the distillation under reduced pressure of a mixture of a perchlorate and sulphuric acid or of a crude perchloric acid that has been prepared by the decomposition of aqueous chloric acid by heat, by the action of sulphuric acid upon barium perchlorate, or by the action of hydrofluosilicic acid upon potassium perchlorate.

---

[1] NOTE.—This investigation was the result of a search for a cheap and convenient method for the preparation of perchloric acid, to be used in making perchlorate baths for the electroplating and refining of metals as described in the United States Patent, No. 931,944, issued to the author.

Kreider[1] has described a method which avoids this troublesome distillation under reduced pressure, which is easy of manipulation and which gives a very pure perchloric acid. His method is based upon the reaction expressed by this equation:

$$NaClO_4 + \text{conc. } HCl\ (+\ \text{excess conc. } HCl) = NaCl + HClO_4.$$

Solid dry sodium perchlorate is treated with an excess of concentrated hydrochloric acid. The mixture is then filtered and the residue of sodium chloride which is almost insoluble in the excess of hydrochloric acid is washed with concentrated hydrochloric acid. The filtrate is a mixture of perchloric acid, hydrochloric acid and small amounts of the sodium salts of these acids due to the slight solubility of the sodium chloride in the hydrochloric acid solution. By heating this filtrate until white fumes of perchloric acid are evolved, the hydrochloric acid is volatilized and the perchloric acid remains behind. The boiling points of the hydrochloric acid and the perchloric acid with 2 molecules of water (119 and 203° respectively) are so far apart that a very satisfactory separation is obtained.

The object of this research was to determine the best conditions and the proper quantities of reagents to use in order to obtain the best results from this process of Kreider, since the original article only gave a qualitative description of the method.

Twenty grams of sodium perchlorate (weighed to 1 mg.) was placed in a 100 cc. beaker and treated with the concentrated hydrochloric acid. The contents of the beaker were filtered upon a Gooch crucible and the residue of sodium chloride washed with ten 1 cc. portions of concentrated hydrochloric acid. The filtrate, which contained the aqueous perchloric acid and the excess of hydrochloric acid together with small amounts of the sodium salts of these acids, was evaporated upon a hot plate to volatilize the hydrochloric acid. The residue which did not volatilize below a temperature of 150° consisted of aqueous perchloric acid whose purity and yield depended upon the conditions of the experiment. These samples of perchloric acid were analyzed to determine the free perchloric acid, the sodium perchlorate and the hydrochloric acid. The residues of sodium chloride that were obtained by the first filtration upon the Gooch crucibles, were analyzed to determine the sodium perchlorate.

Methods of Analysis.—Free acids were determined by titration using methyl orange as indicator. The end point with perchloric acid was decisive and satisfactory. Volhard's method was used for the volumetric determination of the chlorides. The perchlorates in the free perchloric acid were determined by evaporating a measured portion to dryness in a platinum dish. The dish was then heated to near redness until the perchlorates were decomposed to chlorides. The end of this decomposition was easily detected since the perchlorates were easily fusible and the chlorides were infusible at this temperature. The total residue which consisted essentially of sodium chloride was calculated to sodium perchlorate. Of course this method would only correct results with samples containing perchloric acid, sodium perchlorate and easily volatile substances such as hydrochloric acid. The estimation of perchlorates in the presence of chlorides depends upon the determination of the difference between the chlorine in a sample that has been treated to decompose the perchlorates into chlorides and in an untreated sample. This decomposition can be accomplished very easily by the method of Dittrich and Hollenback.[1] The perchlorate is fused for several hours with sodium nitrite. After cooling, the fused mass is dissolved in water and the chlorine is determined by the method of Volhard. Porcelain dishes are attacked by the fused sodium nitrite so platinum vessels must be used. The sodium nitrite that was used in this research contained chlorine so a blank was determined and the proper correction was applied to each analysis. This method gave uniformly accurate results and was satisfactory in every way.

---

[1] Kreider, *Am. J. Sci.* [3], 49, 443; *Z. anorg. Chem.*, 9, 343. Treadwell and Hall, "Quantitative Chemistry," Vol. 2, page 47 (1904).

Materials Used.—A commercial preparation of sodium perchlorate was used. Its composition was: NaCl, 1.76, 1.86; $NaClO_4$, 95.38, 95.77 per cent.; $NaClO_3$, trace.

Commercial barium perchlorate was used. The material was "caked" in the bottle and an average sample for analysis was difficult to obtain. An analysis showed 53.5 per cent. of ClO_4. The C. P. hydrochloric acid which was used showed a specific gravity (spindle) of 1.16 at 24°. The commercial acid which was used in one experiment had a specific gravity of 1.14 at 24°, and each cc. contained 0.00097 gram of non-volatile matter.

TABLE I.—EFFECT OF WATER

The sodium perchlorate (20 grams) was dissolved in 7 cc. of water at 105° and then 20 cc. concentrated hydrochloric acid was added. For comparison the results without water are included in this table.

Grams water added. cc.	$HClO_4$ in the filtrate in terms of $NaClO_4$.		$NaClO_4$ in filtrate. Grams.	Total ClO_4 in filtrate. In terms of $NaClO_4$.		$NaClO_4$ in NaCl residue. Gram.
	Grams.	Per cent.		Grams.	Per cent.	
7.0	15.48	81.6	2.63	18.11	94.7	0.2
0.0	16.97	88.4	1.65	18.62	97.4	0.46

---

[1] Dittrich and Hollenback, *Ber.*, 38, 751 (1905).

This data shows that water should not be added.

TABLE II.—EFFECT OF THE QUANTITY OF HYDROCHLORIC ACID.

Cc. of HCl.	$HClO_4$ in the filtrate In terms of $NaClO_4$		$NaClO_4$ in filtrate.	Total ClO_4 in filtrate. In terms of $NaClO_4$.		$NaClO_4$ in NaCl residue.
	Grams.	Per cent.	Grams.	Grams.	Per cent.	Grams.
10	13.65	71.4	1.91	15.56	81.4	2.72
15	15.4	80.5	1.61	17.05	89.2	1.46
20	16.97	88.4	1.65	18.62	97.4	0.46
25	18.13	94.8	0.84	18.97	99.2	0.2
30	18.35	96.0	0.79	19.14	100.1	0.18
50	18.65	97.6	0.63	19.28	100.8	0.34

This table shows that 25 to 30 cc of hydrochloric acid should be used for each 20 grams of sodium perchlorate.

TABLE III.—TO FIND THE TEMPERATURE NEEDED TO EXPEL THE HYDROCHLORIC ACID FROM THE FILTRATE.

Temperature.	Cl in the filtrate. In terms of $NaClO_4$. Grams.
120°	2.006
130°	0.06
135°	0.0
145°	White fumes of $HClO_4$.

The filtrates containing the perchloric and hydrochloric acids were heated upon a hot plate. The sides of the beaker should be brought to the temperature of the experiment since, otherwise, the drops of the liquid which condense upon the upper part of the beaker retain hydrochloric acid. When the temperature of the entire beaker was brought to 135° there was not enough hydrochloric acid remaining to give an opalescence with silver nitrate. All of the hydrochloric acid could probably have been removed by maintaining the temperature somewhat below 135° for a period of time but this experiment was not tried. This table shows that all of the hydrochloric acid is volatilized at a temperature of 135°.

TABLE IV.—LOSS OF PERCHLORIC ACID DURING THE VOLATILIZATION OF THE HYDROCHLORIC ACID.

Volume of aqueous $HClO_4$ used.	Cc. of substances added.		Grams. of $HClO_4$ present.	$HClO_4$ lost.	
	H_2O.	HCl (conc.).		Gram.	Per cent.
40	0	..	6.97	0.09	0.13
40	50		6.97	0.14	0.20
40		90	6.97	0.19	0.27

The solutions were heated upon the hot plate until the temperature reached 135°. Any loss as small as that shown in this table can be neglected in a method of preparation.

TABLE V.—AMOUNT OF WASHING NEEDED TO REMOVE THE PERCHLORIC ACID FROM THE SODIUM CHLORIDE RESIDUES.

The residue was first drained by suction. It was then washed with 5 1 cc.-portions of concentrated hydrochloric acid, again drained by suction, then washed with a second five 1 cc.-portions of acid, etc. Each five 1 cc.-portions were saved separately and analyzed.

Conc. HCl used in washing	$HClO_4$ washed from the residue of NaCl. Grams.
First 5 1 cc.-portions	large amounts.
Second 5 1 cc.-portions	1.65
Third 5 1 cc.-portions	0.19
Fourth 5 1 cc.-portions	0.08

After washing with twenty portions of acid, 0.06 gram of sodium perchlorate still remained in the residue. This table shows that ten 1 cc.-portions of concentrated hydrochloric acid is the most economical amount to use in washing the residue from 20 grams of sodium perchlorate and 25 cc. of concentrated hydrochloric acid.

In one experiment 20 grams of barium perchlorate were treated with 60 cc. of hydrochloric acid. The precipitate of barium chloride was very bulky and voluminous, entirely filling an ordinary Gooch crucible. The 60 cc. of hydrochloric acid just made the residue liquid enough so that it could be poured upon the filter. The yield of perchloric acid was 80.9 per cent. of theory. Washing with ten 1 cc.-portions of hydrochloric acid failed to wash the perchloric acid out of such a bulky residue. Another experiment showed that "commercial" hydrochloric acid did not give as good results as the "C. P." acid. This was no doubt due to the lower concentration of the "commercial" acid. The yield of perchloric acid was 88.7 per cent. as compared to 96.0 per cent. for the "C. P." acid. Potassium perchlorate cannot be used.

Summary.

These experiments were made to determine the best conditions for the preparation of perchloric acid by the action of concentrated hydrochloric acid upon sodium perchlorate.

The sodium chloride is insoluble in the excess of concentrated hydrochloric acid and can be separated from the perchloric and hydrochloric acids by filtering upon an asbestos filter and by washing with concentrated hydrochloric acid. By heating the filtrate, the hydrochloric acid can be volatilized away from the perchloric acid. The best conditions are: Use 25 to 30 cc. of concentrated hydrochloric acid for each 20 grams of sodium perchlorate. Do not add any water to the substances. Filter out the sodium chloride residue and wash with ten 1 cc. portions of concentrated hydrochloric acid. Heat the filtrate and washings to 135° to volatilize the hydrochloric acid. The yield of perchloric acid is about 95 per cent. of the theoretical. Only about 1 per cent. of the sodium perchlorate is lost in the sodium chloride residues. The other 4 per cent. is in the perchloric acid as sodium perchlorate. The perchloric acid is free from chlorides. The process does not work with potassium perchlorate and is unsatisfactory with barium perchlorate.

UNIVERSITY OF INDIANA, BLOOMINGTON.

ORGANIZATION OF INDUSTRIAL RESEARCH.[1]

BY WILLIS R. WHITNEY.

Received November 6, 1909.

The intimate connection between the purely scientific research of a people and its advance in the art of good living cannot be too frequently discussed. The organization of industrial research involves arranging and maintaining a body of involute parts as an operative whole of highest efficiency. It is never perfectly accomplished, and the fact that improvement can always be made is an incentive for its discussion.

A recent copy of *Life* has this to say, which, without straining, bears directly upon industrial research:

"This is the most interesting country in the world. The game here is the biggest that is being anywhere played. The problems of humanity that are being worked out here are the greatest problems under consideration, and the prospect of solving them is better than it is anywhere else."

Lord Bacon said: "The real and legitimate goal of the sciences is the endowment of human life with new invention and riches." He, in turn, cited King Solomon, who said, "it is the glory of God to conceal a thing, but the glory of a king to search it out."

Bacon distinguishes three degrees of ambition:

First, that of men anxious to enlarge *their own* power *in* their own country. This is "vulgar and degenerate."

Second, that of men who strive to enlarge the power and empire of their *country* over mankind. This is "more dignified, but not less covetous."

Third, that of those who strive to enlarge the power and empire of *mankind* in general over the *universe*. Evidently this is the best, and is the real ambition, whether recognized or not by himself, of any good experimenter.

For purposes of systematic analysis, the subject, "Organization of Industrial Research," may be divided into two parts:

Part one, the personal or mental organization, with its requirements, etc.

Part two, the objective or material organization.

For brevity, these may be called the mind and the matter organizations.

The former, or personal, I will subdivide into such parts as:

Its training and characteristics.

Division of its labors.

Its records, etc.

The objective or matter organization, I divide into:

---

[1] An address delivered at the Twentieth Anniversary of Clark University, Sept. 17, 1909.

The fields for material research.

The laboratory equipment and systems of its material co-operation.

Naturally, the personal comes first, relatively and chronologically, and the mental precedes the material. The personal factor is *everything* in industrial research. Strangely enough, it is everywhere and always dominant, while every other factor is sometimes recessive. In an organization "A" cannot work well with "B" because one is too slow, too fast, to egotistical, too jealous, too narrow, etc. Nowhere else do the personal traits protrude so much as in concerted research And so I hold that above all, as an industrial experimenter, I should like as broad a *human* training as possible, before any other specific one This probably means little more than acquirement of a *demonstrated* desire to play fair, and it may be no more applicable to this field than to others.

To one always in close touch with research, it seems as though there is an immutable law of nature which may be stated as follows: (It is an application of the principle of reversible reactions so as to include the reactions of the mind.)

The equilibrium between mental and material conception is so sensitive that anything which, to the fair mind, seems possible, is to the trained persistence permissible. If this should be proven not strictly true, it would still be a good working hypothesis for a research organization.

This theory requires, then, a certain characteristic in the generally successful research operator. This is recognized in *optimistic activity* and, to my mind, should be placed first among the requisites It is placed above *knowledge*, because, without it, little that is new will ever be done except by accident. With active optimism, even in absence of more than average knowledge, useful discoveries are almost sure to be made.

Speaking from personal analysis and from the observation of others, I would say that general-chemical and physical knowledge may sometimes be as much a detriment as a help to one imbued *only* with a *need* of solving new problems. A possible explanation is this: We always reason deductively. We apply general laws in attempting to answer specific questions. To any specific problem of research there are usually general laws which may seem to forbid the solution. These laws are known and revered. Naturally, the unknown, specific ways by which it may be solved are more or less hidden An illustration may not be out of place here:

Cotton may be dissolved in a solution of zinc chloride. The solution may be squirted through a die into alcohol in such a way that a smooth, coagulated cellulose thread is thereby obtained. This may be heated so as to give a solid, compact and pure carbon filament. Many are thus made. But as a new problem, it would certainly appear quite impracticable to one who might have a fairly extensive knowledge of the chemistry of the materials. Generally speaking, zinc chloride solution does *not* dissolve cellulose. Only a strong solution, kept at a high temperature for a long time, will give the desired solution. In general, too, it could *not* be squirted and coagulated into a smooth thread. Very specific conditions are necessary. Finally, the treatment with gradually rising temperature, which alone succeeds in giving the compact carbon filament, is a matter of specific detail. The places in this process where general reasoning points to failure are numberless. Years of multiplied effort are necessary to perfect such a process. Once established, it is easily analyzed along the lines of understood reason and theories of reactions may be based upon the facts. But such processes are not laid out greatly in advance of their accomplishment. The successful steps are found among the many which are actually attempted, and something more than general knowledge is necessary. This something is hopeful pertinacity, optimistic activity. To a chemist imbued with fair knowledge, it was recently apparently useless to attempt such an experiment as the continual removal of traces of hydrogen from oxygen by passing the gas through a red-hot iron pipe. He had seen iron wire burned rapidly in oxygen, he tried wrought iron and the iron was oxidized, and his knowledge was vindicated, but he also tried cast iron and found that it did not burn and that it would operate perfectly. A scramble for an explanation evolved the theory that the silicon burning to silica protected the iron. *Ex. postfacto* theories are permissible.

As the mental world is constituted, optimists are greatly in the minority, when one counts those only who are also imbued with knowledge. Therefore, in practice, the optimist must be used to crystallize the efforts of others less optimistic. Thus, any large industrial research laboratory is soon *perforce*, systematized into organized clusters of people, working along distinct and different lines. This permits, in our case, of the combined use, to maximum efficiency, of the delicate hands of young women, the strength and skill of trained mechanics, the mind of the useful dreamer, the precision and knowledge of the skilful chemist, and the data of the accurate electrical engineer.

Simple mathematical axioms make clear the fact that a group of operators working together on a subject, are related to the same group operating separately, as a power is related to a simple sum. This principle holds as well among a group of groups and to related subjects. It is evident, for example, that knowledge gained along the line of insulation would be of use in a study of conduction, and that the man who had studied the reduction of tungstic oxide by carbon *in vacuo* could help the one who is working with a pressure furnace, upon the equilibrium between carbon monoxide and carbon dioxide. Therefore, the strength of a research department, properly operated, should rise exponentially with its numbers.

To this audience, the importance of highest advance in specific chemical and physical training will probably be apparent, but an expression of it may be of use. The supply of highly trained men is below the demand. There is a healthy supply of moderately trained men. This applies to all general, scientific training. Let me give more concrete ideas. There are a hundred chemists who can fill satisfactorily an analyst's position, to one who knows what J. J. Thomson has done or who reads Drude's *Annalen*. Reading the *Annalen* is not a "sine qua non," but it is an indicator of no little merit. If a chemist or a physicist is not sufficiently interested to keep informed, he is probably not going to work at high efficiency as an investigator. This does not preclude the possibility of splendid research work being done by some one who is confined to a very limited field of vision, but such cases are the exception and cannot be used as bases for common application. In general, the man with the best tools and with the best knowledge and experience in their use, will advance most rapidly in industrial research. In my own experience, we frequently have a line of work which demands the addition to the force of well trained men. The difficulty which stands out most markedly when considering this problem is usually the scarcity of men who are highly enough trained along the line of pure research. While in many fields of *industrial* research new and brilliant discoveries will continue to be made suddenly and, as it were, out of new cloth, still many more are being made by the most careful application of highly refined methods and knowledge, to processes which already seem at first pretty well worked out. This *intensive farming* is most promising and demands the highest skill. It is to-day most difficult to find American trained men who can do this work. It is a German attribute which we would do well to make our own.

If the chemist is only a chemist or the physicist confined to pure physics, he is liable to overestimation of the laws he learns. He should be something of a "mental mixer," one who has enough history, enough psychology, and enough faith to read possibility of acquirement for the future out of knowledge of attainments in the past.

As we have said, one of the most practical detriments to successful industrial research is that automatic action of the mind which recognizes the possible grounds for a failure quicker than it sees the probable ways to success. Research needs more aviators. Those of us who feel the work-horse brand on our work have a call to cultivate a *flying* spirit, and are to be condemned only if we stand still.

In this connection, I am in favor of anything which helps train the American student in the path of sanguine research. It can be done by research men themselves, but probably not by others. It is not the *knowledge* which the student preparing for research needs, so much as the spirit of the investigator. His thoughts should not be fettered by laws, but helped by them to fly. This can be done best by those who are optimistic almost to the extinction of reason.

A search in the research laboratories of the world to-day would disclose large numbers of J. J. Thomson men, Ostwald men, Nernst men, van't Hoff men The teacher probably made the school. The investigator probably endowed the students, not with facts alone, but with spirits. We are not of that hopeless class who assume that the sparks of genius are only Heaven-sent, but we are inclined to adopt as an axiom that man is flexible, auto-corrigible and mentally elastic beyond limit. Therefore the rare genius in research, as elsewhere, is the one most given to hopeful effort.

To dwell for a moment upon points in a system for co-operation of a research force, I will describe our own scheme.

The present corps comprises about eighty people, about thirty of whom are college men, mostly chemists. Every man or woman on the research staff is expected to give undivided effort to the work. Whatever invention results from his work becomes the property of the company. I believe that no other way is practicable. An attempt to reward systematically such labors by a scheme of royalty payment is more impracticable than the operation of a manufacturing plant upon a graded scheme of profit sharing. In this case an immediate and fairly equitable division of profits is sometimes possible. In research, the problem itself is an asset of the organization. Both the equipment and the risks belong to the organization. The accumulated experience of the force as a whole is its property. Finally, the privilege of directing the work of operators along lines where no direct financial benefit (or an immeasurable one) to the company could ever be determined, must belong to it. Every operator is expected to keep good notes and his books become a part of the laboratory files. In most cases weekly typewritten reports are made by each worker, and copies of these also become part of accessible library files. For purposes of establishment of dates, etc., witnesses who read and understand the notes also endorse them. Photographs of apparatus, curves, etc., are frequently added wherever useful, and each room of the laboratory is photographed regularly and the dated photographs are bound in books, to record standing conditions. Wherever practicable, single sheets, of standard report size, are printed to cover oft-repeating data, so that the experimenter regularly fills in certain blanks, as, for example, in experiments on carbon motor brushes: the composition of the particular lot, temperature and time of drying and firing, hardness, resistivity, tensile strength, and all other tests of the product. The use of plotted curves on standard millimeter paper, for use where one property of material is studied as a function of some other variable, is very common in our reports. This occurs, for example, in practically all cases where electric furnace work is described, and where the changes undergone by incandescent lamps during their life are recorded.

These conditions are the result of eight years of development. The system has been subjected to many changes and may still be greatly improved. It is possible to have such a complex system of record that efficiency is sacrificed. We have reached the present stage because of frequent indications of previous weakness in the simpler methods. Very few good investigators can keep good notes. The more interested the investigator becomes, the more difficult it seems for him to carefully record his passing work. His eyes and mind are always upon the exciting and more interesting advance. It seems not so tempting to actually make history by the writing as to metaphorically make it by the conception or experiment.

We now come to the material side of the subject.

In the early days, the same hands which mined the iron ore and operated the bellows, also forged the sword and plowshare and touched the goods which were the equivalent in exchange. The records of the development through which the distribution of the steps of such processes has gone is what we call the history of man. It is not always easy to recognize the extent to which this development is progressing in our own time. Statistics ought to show us, but these often fail to impress us. It may be that if used to a limited extent to armor an argument, a few data will be of interest in connection with industrial research.

The known chemical compounds of the earth are myriads. The still unknown, but knowable, are certainly many myriads more, but any consideration of either great mass is too huge a task. We may, however, consider for a moment a part of the alphabet from which that language is made. We will consider research as applied to the *metallic elements* alone.

There are about 75 elements. About two-thirds are metals. Of these, only a very few can be said to have been the subject of much industrial research. It is impossible to accurately measure the extent to which an element has been studied with a view to its possible use by the race, but we have no difficulty in recognizing that iron and copper have been much studied, while calcium and silicon have not. In these illustrations we have *not* selected *rare* elements. The calcium and silicon, which have been least used by man thus far, are more common than copper or iron. A natural explanation of the lack of development of such elements is a lack of need, but this is possibly incorrect. Copper, iron, etc., were certainly first obtained by accident as distinct from design. The uses to which they could be put were later developed by trial. The finding of some uses established the further supply, which insured the subsequent discovery of new uses. This mirrors the history now being made by new elements such as silicon. Only in the past year the commercial production of this element has been begun, and about 500 tons were sold for a deoxidizer in steel-making. Thus a substance absolutely out of reach of almost every chemist a few years ago, can now be obtained as cheaply as zinc.

Similarly, future needs, which only calcium, for example, can meet, are certain to be developed. More calcium will then be made. The cost of production will be reduced and the field of its usefulness will again and ever afterward continue to broaden. Never in the history of the world has the rate of iron production been so great as at present (nearly two million tons a month by the U. S. Steel Company alone). Copper is being mined more rapidly than ever before. We have ourselves seen the industrial birth and growth of a new metal which points to the great possibilities in case of the other unused elements. I refer to aluminium. Only two to three tons were made as late as 1884 while furnaces now exist which are capable of yielding three to four times this quantity every hour of the day and night. Its *present* uses could only have been, and were, very imperfectly predicted, before actual industrial research made tentative use of it. So it must be with other elements. One is not too bold who assumes that all the elements which are found in abundance will be industrially utilized when they have been economically isolated and thoroughly investigated.

I am considering the metallic elements only in order to point out in a concrete manner the need of high-quality research, physical, chemical, electrical, etc., in the *simplest* field. Evidently this field, among compounds of the elements, is again bounded only by the infinite. I am impressed with the idea that the commonest elements in nature have not been *studied* with anything like the care which has been given to those for which the demands are already developed.

In our age, a single investigator will probably not isolate, in large quantities, the metal tellurium, for example, and also put it to use to fill one of his individual needs, as did the warrior who first fashioned an iron blade or axe. The men who develop the myriad uses to which the common element titanium will be put, will have to rely upon the previous work of many investigators. It is in this respect that the conditions are continually changing, and always in one direction. I call it the direction of specific complexity. Our wants are very complex. We are learning to demand very specific properties. It is this fact which makes necessary the research work of the specialist, the specific or narrow investigation of the pure scientist, the pioneer work of the trail-blazer, the crude and hurried trials by the inventor, the long and exacting developments of the practical application in the factory, etc. Demands for new materials do not really precede the discovery of the product, any more than the demand for high-speed tool steel preceded the discovery of the properties of the chrome-tungsten-iron alloys. With the material discovered, its properties known, the world apparently could then hardly get along without it. This means that necessity is not the mother of invention. Knowledge and experiment are its parents. It sometimes happens that a successful search is made for unknown material to fill well recognized and predetermined requirements. It *more* often happens that the acquirement of knowledge of the previously unknown properties of a material suggests its trial for some new use. These facts strongly indicate the value of knowledge of properties of materials and indicate a way for research.

Among the recently developed uses for modern metals which were certainly not surmised until the metal itself had been made easily available, are the use of aluminium and silicon as deoxidizers in steel-making, where all the silicon and a large part of the aluminium are now used. This discovery of utility by experiment, rather than the discovery of material by *force of necessity*, is again illustrated by the metals titanium and vanadium. The former is used in arc lamps because it was found, by experiment, to give a good light. (Your Worcester streets are lighted by it.) The latter has been surprisingly useful in steel-making, where a fraction of 1 per cent. has been found to impart additional strength to the steel. In this way, about a thousand tons of vanadium are now used annually in America.

When the first step is taken from the study of the supply, production and utilities of our metallic elements, the next step is apparently along the lines of alloys and we readily see how quickly the field widens. The recent great advances in scientific foundation for much study are to be attributed to the physical chemists, to such men as Tamman and his school. In their work we begin to see the magnitude of the alloy field. There are probably over a *thousand pairs* of metals whose properties as alloys are still absolutely unstudied, and for alloys of three or more metals the number is legion.

It seems as though our advance could be quickened by a greater intimacy with the newly cheapened elements. When sodium, chlorine, bromine, silicon, magnesium, chromium, cobalt, manganese, tungsten, etc., etc., are many times as available or cheap as they were only ten years ago, it is probable that the possible uses are not up-to-date.

The field of material research really divides into two parts: the search for more economical production and the search for wider application. These two go hand in hand. If the one advances, the other is led along. In this way, in our laboratory, the knowledge of such elements as carbon, as in its forms of graphite in lamp filaments, in motor brushes, in electrodes, etc., has been widely and continually advanced. The result is not a conclusion that we know all about carbon, but rather that it still presents a wonderful field for useful research.

From the materials worked *upon*, to the tools is a step. Our experience here is concrete and clear, and we want to record our impressions. Good tools, new tools, rare tools, are most valuable. No good tool lives long for a single use alone. Many times we have questioned the advisability of installing some new apparatus—a vacuum furnace, a pair of metal rolls, some special galvanometer, some microscope, an hydraulic press, a power hammer, a steam digester, etc., etc. Never, after it became a part of the equipment, has it seemed possible to proceed without it. In the single case of the electric vacuum furnace, for example, our laboratory has made almost continual use of from three to eight for the past five years. The laboratory, piped several years ago with high vacuum and with electrolytic hydrogen, besides steam, air, water and gas, will probably never operate without them.

Similarly, this applies to a library. In general, the most useful and fertile of our investigators use the library the most. This is as it should be. The recorded research work in a library of a few thousand volumes frequently represents the work of millions of work-hours, and there is little excuse for not availing oneself of the published experience of others. A library containing ten of the leading research journals of the world may be said to have in each volume about 100,000 available brain-power-hours. So a library corresponds to a charged storage battery of great capacity.

RESEARCH LABORATORY, GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.

NOTE.

The Speedy Detection of Potassium in Small Amounts.—The use of sodium cobaltinitrite as a reagent for the detection of potassium has been known for a long time, but very little attention appears to have been given to its delicacy. Crookes[1] quotes De Koninck as saying that the precipitate is still formed at a dilution of 1/1000 KCl, but not at 1/2000. The writer also obtained by an indirect method the proportion of 1/1600 K_2O as the point at which precipitation would not occur.

A careful investigation of this reaction is given by W. C. Bray,[2] who finds the sensitiveness to be far greater than the above figures. During the course of a study of this reaction for quantitative purposes, the writer was fortunate enough to find a means of greatly shortening the time required for the test. Bray dissolves a given amount of potassium as potassium chloride in 5 cc. of water, adds a little acetic acid and 5 cc. of the sodium cobaltinitrite reagent (containing 0.5 g. Co in 100 cc.), then allows it to stand until there is a turbidity formed, afterward bringing the precipitate onto a white filter paper where it can be easily seen. The writer has found that if to the solution prepared as described there be added an equal volume of strong alcohol the precipitate will be formed in a very short time, so short in fact that if enough potassium is present to give a test at all it will by this means be thrown down in a few minutes, where several hours would be required otherwise. The following table shows the comparative times required by the procedure used by Bray and that where alcohol is added.

---

[1] "Select Methods in Chemical Analysis," 1.

[2] THIS JOURNAL, 31, 621, 633 (1909).

Without alcohol.				With alcohol.			
Mgs. K.	Pts. per 100,000.	Turbid in.	Precipitate settles in.	Mgs. K.	Pts. per 100,000.	Turbid in.	Precipitate settles in.
...	....	....	....	0.1	20	immed.	at once
0.5	10	1–4 min.	short time	0.5	10	immed.	at once
0.3	6	1–4 min.	short time	..	...	......	....
...	....	....	....	0.25	5	immed.	5 min.
0.2	4	20–30 min.	2 hrs.	0.2	4	3 min.	6 min.
0.1	2	6–10 hrs.	not given	0.1	2	4 min.	11 min.
...	....	....	....	0.05	1	......	....
...	....	....	....	0.01	0.2	......	....
0	0	....	....	..	...	......	....
0	alcohol added	....	....	0	...	......	....

This shows that the sensitiveness of the reaction is not increased by the addition of alcohol, but that any potash that will be detected at all will be shown in a few minutes. A qualitative test, however, sensitive to 2/100,000 is unusual, and is really more accurate than needful in ordinary work

Particular care must be exercised to insure the removal of all ammonium salts previous to testing for potassium, since by the addition of alcohol they are thrown down as quickly as the latter, and almost as completely. This reagent gives a sensitiveness with ammonium salts of 5/100,000, making it not greatly inferior in point of delicacy to the Nessler reagent. Following is given a comparison of Bray's results on ammonium salts and mine where alcohol is added.

Without alcohol.			With alcohol.		
Mgs. NH_3.	Pts per 100,000.	Turbid in.	Mgs. NH_3.	Pts. per 100,000.	Turbid in.
2	40	at once	..	...	.....
1	20	10 min.	1	20	immed.
0.5	10	several hrs.	0.5	10	immed.
...	..	....	0.25	5	immed.
...	..	....	0.1	2	none
...	..	....	0.05	1	none
...	..	....	0.01	0.2	none

L. T. BOWSER.

OHIO AGRICULTURAL EXPERIMENT STATION,
WOOSTER, OHIO.

CORRECTION.

My attention has been called to an error in the review of recent work in inorganic chemistry, which appeared in the December number of THIS JOURNAL. The statement is made that Keiser found the formula of the bicarbonates of calcium and barium to approach "closely the formula $H_2M(CO_3)_2$." As a matter of fact the bicarbonates analyzed contain considerably more carbonic acid than would correspond to this formula, being in the case of the calcium salt $CaCO_3.1.75H_2CO_3$, and in the case of barium $BaCO_3.1.5H_2CO_3$. The work should also have been attributed to Keiser and Leavitt, and Keiser and McMaster. JAS. LEWIS HOWE.

[CONTRIBUTION FROM THE WELLCOME CHEMICAL RESEARCH LABORATORIES, LONDON.]

CHEMICAL EXAMINATION OF JALAP.[1]

BY FREDERICK B. POWER AND HAROLD ROGERSON.

Received November 8, 1909.

Under the title of *Jalapa* (Jalap) the various national Pharmacopoeias recognize the dried tuberous root of *Exogonium purga*, Bentham (*Ipomoea purga*, Hayne). The only constituent of the tuber possessing chemical interest is the resin, which is largely used medicinally. This resin (*Resina Jalapae* of the Pharmacopoeias), like many similar products obtained from plants belonging to the family of Convolvulaceae, is of a glucosidic nature. It has been the subject of numerous chemical investigations during the past century, and the literature relating thereto is therefore considerable in extent. A review of the more important of these publications has been given by Hoehnel[2] in connection with an investigation entitled "Ueber das Convolvulin, das Glycosid der Tubera Jalapae (*Ipomoea purga*, Hayne)." A quite complete account of this subject and of other closely related so-called glucoside resins, together with citations of the literature, have also been recorded by van Rijn ("Die Glykoside," Berlin, 1900), and by Tschirch ("Die Harze," Bd. II, Leipzig, 1906).

It would not be expedient in this place to consider in detail the various statements of earlier investigators respecting the composition of jalap resin or the products obtained therefrom, especially as many of these statements are not only conflicting, but are evidently based upon incorrect observations and deductions. In order, however, to indicate the unsatisfactory state of present knowledge respecting the chemical characters of this resin, a brief exposition of the subject may be given.

The chief portion of jalap resin, which is insoluble in ether and commonly designated as "convolvulin,"[3] although a completely amorphous product, has at various times been assigned the following empirical formulas: $C_{31}H_{50}O_{16}$ (Mayer); $C_{21}H_{35}O_{10}$ (Kayser); $C_{24}H_{40}O_{12}$ (Laurent);

---

[1] Communicated, in abstract, to the International Congress of Applied Chemistry, London, June 1, 1909. Presented at the meeting of the New York Section of the American Chemical Society, October 30, 1909.

[2] *Arch. Pharm.*, 234, 647 (1896).

[3] In English pharmacy the portion of jalap resin which is insoluble in ether is still frequently designated by the original and more appropriate name of "jalapin." The latter term, however, is now more commonly employed to denote the resin of scammony and of Mexican Male jalap (*Ipomoea orizabensis*, Ledanois), both of which are completely soluble in ether.

$C_{32}H_{62}O_{16}$ (Taverne); $C_{61}H_{108}O_{27}$ (Kromer); $C_{54}H_{96}O_{27}$ (Hoehnel). It has been stated by the last-mentioned investigator,[1] whose results alone need be somewhat further considered, that "convolvulin," when treated with bases, yields the following products: methylethylacetic acid; "purgic acid;" and "convolvulic acid." Purgic acid, which has been regarded as dibasic, and possessing the formula $C_{25}H_{46}O_{12}$, has been described as forming a yellowish, extremely hygroscopic, varnish-like mass, readily soluble in ether. Convolvulic acid, which is insoluble in ether, and was regarded as monobasic, was obtained as a white, amorphous powder, to which the formula $C_{45}H_{80}O_{28}$ was assigned. Both of these products were found to be glucosidic, the purgic acid, when heated with dilute mineral acids, having yielded a sugar, a product regarded as decylenic acid, $C_{10}H_{18}O_2$, and hydroxylauric acid, $C_{12}H_{24}O_3$, while convolvulic acid, by the same treatment, yielded a sugar and convolvulinolic acid, $C_{15}H_{30}O_3$. In the latter instance it was assumed that the hydrolysis might be represented by the following equation:

$$C_{45}H_{80}O_{28} + 5H_2O = 5C_6H_{12}O_6 + C_{15}H_{30}O_3$$

A consideration of the results obtained in the present investigation will doubtless render it evident that many of the conclusions which have previously been recorded respecting the composition of jalap resin and various amorphous products obtained therefrom are erroneous. In the first place, it would be quite fallacious to assign to the so-called "convolvulin" any empirical formula whatsoever, inasmuch as we have shown that by successive extraction with various solvents, such as chloroform, ethyl acetate, and alcohol, it may be further resolved into several products, all of which, moreover, are amorphous and of indefinite composition. Similar conditions exist with regard to the character of the amorphous products obtained by the alkaline hydrolysis of the resin, such as the so-called "purgic" and "convolvulic" acids, to which empirical formulas have likewise been assigned. Both of the last-mentioned products are complex mixtures, some of the constituents of which are not even glucosidic. We have shown, for example, that the alcohol extract of the resin, when hydrolyzed by baryta, yields a product which, like the original resin, is capable of being further resolved when successively extracted with ether, chloroform, ethyl acetate, and alcohol. The last-mentioned alcohol extract, when heated with dilute sulphuric acid, affords, moreover, not only sugar and convolvulinolic acid, $C_{15}H_{30}O_3$, as indicated by Hoehnel in the case of a less completely purified product, but also ipurolic acid, $C_{14}H_{28}O_4$, and several volatile acids, while a portion of it apparently remains unchanged. It is thus obvious that the "convolvulic acid" of Hoehnel can not be regarded as an individual substance, nor can its degradation be represented in the manner suggested by him.

---

[1] *Loc. cit.*

Notwithstanding the numerous investigations of jalap resin, it will be apparent from the observations above noted that the statements concerning its composition and character are not only widely divergent, but that in many respects they are based upon quite erroneous assumptions. It has therefore been deemed desirable to subject this resin to a more complete examination, and the results of the present research are summarized at the end of this paper.

Experimental.

The material employed in this investigation consisted of an original bale of Jalap tubers of good quality, as indicated by the percentage yield of resin when assayed by the methods described below.

As a preliminary experiment, 50 grams of the finely ground material, representing an average sample of 75 kilograms of the drug, were successively extracted in a Soxhlet apparatus with various solvents, whereby the following amounts of extract, dried at 100°, were obtained.

	Gram.		Per cent.
Petroleum (b. p. 40–60°) extracted	0.19	=	0.38
Ether "	0.34	=	0.68
Chloroform "	0.27	=	0.54
Alcohol "	5.90	=	11.80
Water "	11.15	=	22.30
Total,	17.85	=	35.70

Determination of Total Resin.—I. The first method employed in this determination was essentially that of the British Pharmacopoeia. Fifty grams of the finely ground material were thoroughly extracted in a Soxhlet apparatus with hot alcohol (94 per cent.). To the liquid thus obtained 25 cc. of water were added, and the alcohol removed by distillation, after which the residue was brought into a dish and heated on a water bath in order to remove the last traces of alcohol. The separated resin was then thoroughly washed with hot distilled water, and finally dried in a water oven until of constant weight. Two concurrent determinations yielded 4.7 grams of resin, corresponding to 9.4 per cent. of total resin in the drug. The proportion of this crude resin which was soluble in ether, as determined by its complete extraction in a Soxhlet apparatus, corresponded to 11.6 per cent. of its weight.

II. The second method employed for the determination of the resin was that of the United States Pharmacopoeia (eighth revision), which, however, as in the preceding method, was modified by conducting the extraction of the drug in a Soxhlet apparatus. The amounts of resin, representing the ether extract and the portion insoluble in ether, were

1.0 and 9.5 per cent. respectively, the total resin being thus 10.5 per cent. of the weight of the drug.

It will be observed that the results obtained by the two above-mentioned methods of assay differ appreciably, as might be expected, but the relative merits of these methods need not be here discussed.

Extraction of the Jalap with Hot Alcohol and Distillation of the Extract with Steam.—For the purpose of a complete examination of the drug, 75 kilograms of the ground material were completely extracted with hot alcohol. After the removal of the greater portion of the alcohol, 23.8 kilograms of a soft extract were obtained. A quantity of this extract was brought into a large flask, some water added, and the mixture distilled with steam until volatile products ceased to pass over. A distillate was thus obtained, which contained some oily drops floating on the surface. After this operation there remained in the distilling vessel a dark colored, aqueous liquid (*A*) and a quantity of soft resin (*B*). The resin was repeatedly washed with warm water until the latter remained colorless, and the washings added to the aqueous liquid.

Examination of the Steam Distillate. Separation of an Essential Oil.

The distillate obtained as above described was extracted with ether, the ethereal liquid being dried with anhydrous sodium sulphate and the solvent removed. A very small amount (2.4 grams) of an essential oil was thus obtained, which, when distilled under diminished pressure, passed over between 80 and 160°/60 mm. This oil, when freshly distilled, had a pale yellow color, but became very dark on standing. It possessed a disagreeable and persistent smoky odor. A dilute alcoholic solution of the oil gave with ferric chloride a deep brownish red color. Its density was 0.8868 at 20°/20°, and it was optically inactive.

Examination of the Aqueous Liquids (A).

The aqueous liquid remaining in the distillation flask, after the above-described treatment with steam, was separated from the resin, and, together with the washings from the latter, evaporated to a small volume. As the dark colored sirup thus obtained deposited nothing on standing, it was diluted with water, and a solution of basic lead acetate added until no further precipitate was produced.

Basic Lead Acetate Precipitate.—This was collected, thoroughly washed with water, and then suspended in water and decomposed by hydrogen sulphide. After filtration, the liquid was concentrated, and shaken with several successive portions of ether. The combined ethereal liquids were repeatedly extracted with a solution of sodium carbonate, and subsequently with a 10 per cent. solution of sodium hydroxide. The first sodium carbonate extracts were dark in color and showed a blue fluorescence. They were acidified and extracted with ether, but the ethereal liquid, on evaporation, yielded only a small amount of an uncrystallizable sirup, which, however, developed with ammonia a blue fluorescence, and gave with ferric chloride a dark green coloration. This fluorescence was evidently due to the presence of a little β-methylaesculetin, a substance which was subsequently isolated in small amount from the chloroform extract of the resin. The extract obtained by means of sodium hydroxide had a dark red color. It was acidified and extracted with ether, but yielded nothing definite.

Filtrate from the Basic Lead Acetate Precipitate.—This was treated with hydrogen sulphide for the removal of the lead, the mixture filtered, and the filtrate concentrated under diminished pressure. It was then repeatedly shaken with ether, and the combined ethereal liquids extracted with several successive portions of aqueous sodium carbonate. The first sodium carbonate extracts had a red color and showed a blue fluorescence. When acidified, and again extracted with ether, a small amount of a sirup was obtained, which deposited a trace of a crystalline substance, but not sufficient to permit of its identification. The sirupy product developed with ammonia a blue fluorescence, and gave with ferric chloride a violet coloration. The ethereal liquid, after extraction with sodium carbonate, was shaken with a 10 per cent. solution of sodium hydroxide, when a dark red, aqueous liquid was obtained. This, however, when acidified and again extracted with ether, yielded nothing definite. The ethereal liquid, which had been completely extracted with the above-mentioned alkalis, was finally dried with calcium chloride and the solvent removed, but only a small amount of a dark red sirup was obtained.

The aqueous liquid which had been extracted with ether, as above described, contained a quantity of sugar, since it readily reduced Fehling's solution and yielded *d*-phenylglucosazone, which, after recrystallization from dilute pyridine, melted at 217–218°. For the further examination of the aqueous liquid it was concentrated to the consistency of a sirup, which, after dilution with alcohol, was mixed with purified sawdust, and the thoroughly dried mixture then successively extracted in a Soxhlet apparatus with chloroform, ethyl acetate, and alcohol. The first two solvents removed but a relatively small amount of material, the larger proportion being subsequently extracted by the alcohol. These extracts were all of a sirupy nature, and, although exhaustively examined, nothing crystalline could be separated from them. They were observed to contain, besides sugar, traces of the fluorescent principle previously referred to, which was evidently β-methylaesculetin.

Examination of the Resin (B).

This product, which had been obtained from the alcoholic extract of the drug as previously described, corresponds to the *Resin of Jalap* of the various national Pharmacopoeias.

Optical Rotation of the Crude Resin.

It has been indicated by P. Guigues[1] that the specific optical rotatory power of certain convolvulaceous resins is a factor which may be utilized for discriminating between them, and for the detection of substitutes and adulterants. This factor was therefore determined for the resin employed in the present investigation with the following result. A quantity of the crude resin was dissolved in 50 cc. of alcohol, and the solution boiled with successive, small portions of animal charcoal until it became practically colorless. The rotation of this liquid in a 1 dcm. tube was α_D —2° 0′, and the amount of substance contained in 10 cc. of the liquid, after drying at 105–110°, was 0.5400, hence $[\alpha]_D$ —37.0°. This result is in fairly close agreement with the figures recorded by Guigues and by Cowie[2] for a decolorized jalap resin, which are $[\alpha]_D$ —36.0 and —37.3° respectively.

Preliminary Extraction of the Crude Resin with Different Solvents.

In order to ascertain the general character of the crude resin, a weighed amount (about 5 grams) was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with various solvents The percentages of extract, dried at 110°, were as follows:

I.	Petroleum (b. p 40–60°)	extracted	1.9
II.	Ether	"	9.7
III	Chloroform	"	24.1
IV.	Ethyl acetate	"	22.0
V	Alcohol	"	38.8
		Loss,	3.5
			100.0

For the purpose of a complete examination of the constituents of the resin, a large quantity of the crude material was employed. This was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted first with ethyl acetate, and subsequently with alcohol. The alcohol extract was then again extracted with ethyl acetate in a similar manner, after which the undissolved material was removed by means of alcohol, this portion being designated as the "alcohol extract of the resin." The entire amount of material removed by ethyl acetate was then mixed with a large quantity of purified sawdust, and the mixture thoroughly dried, after which it was submitted to prolonged successive extractions with petroleum (b. p. 40–60°), ether, chloroform, and ethyl acetate. The extracts obtained by these various solvents, together with the above-mentioned alcohol extract, were then separately investigated.

---

[1] *J. pharm. chim.* [6], **22**, 241, and *Chem. Zentr.*, **1907**, I, p. 309; *Bull. soc. chim.* [4], **3**, 872 (1908). Compare also Power and Rogerson, *Am. J. Pharm.*, **80**, 251 (1908), and Cowie, *Pharm. J.*, **82**, 89 (1909).

[2] *Loc. cit.*

I. *Petroleum Extract of the Resin.*

This extract, after the removal of the solvent, was a very dark colored soft solid. The amount employed for the investigation of its acidic constituents was about 60 grams, but for the examination of the non-saponifiable constituents an additional 60 grams was used.

The extract was dissolved in a large volume of ether, and the ethereal liquid extracted with two successive portions of aqueous sodium carbonate. These alkaline liquids, which possessed a deep red color, were separately acidified, again extracted with ether, and the solvent removed. The product from the first extraction (*a*) amounted to about 12 grams, and that from the second extraction (*b*) to 3 grams. When distilled under diminished pressure, they both passed over for the most part between 220 and 240°/25 mm., and solidified on cooling to a white, crystalline mass. They were then recrystallized from ethyl acetate, and finally from glacial acetic acid, when the product (*a*) melted at 58–60° and the product (*b*) at 60–62°. These products consisted of saturated acids, and they were analyzed with the following results:

(*a*) 0.1804 gave 0.4974 CO_2 and 0.2008 H_2O. C = 75.2; H = 12.4
(*b*) 0.1454 gave 0.4024 CO_2 and 0.1620 H_2O. C = 75.5; H = 12.4
$C_{16}H_{32}O_2$ requires C = 75.0; H = 12.5 per cent.
$C_{18}H_{36}O_2$ requires C = 76.1; H = 12.7 per cent.

It would thus appear that the above-mentioned products consisted chiefly of a mixture of palmitic and stearic acids, the former predominating.

The ethereal liquid which had been extracted with sodium carbonate, as above described, was subsequently shaken with a 10 per cent. solution of sodium hydroxide. This alkaline liquid had a deep red color. It was acidified and extracted with ether, when, after removing the solvent, a small amount of a sirupy product was obtained. The latter deposited a little of a substance in the form of rosettes of needles, which melted at 205–206°, but the amount was too small for further examination.

The ethereal liquid, after extraction with sodium carbonate and hydroxide, was washed with water, dried, and the solvent removed. The residual product, which amounted to 35 grams, was hydrolyzed by heating in a reflux apparatus for several hours with an alcoholic solution of potassium hydroxide. The alcohol was then removed, water added, and the mixture shaken with ether. As an inseparable emulsion was thus formed, the mixture was made slightly acid, then completely extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. This alkaline liquid was acidified, and distilled with steam, when a distillate was obtained which contained a few oily drops floating on the surface. The distillate was extracted with ether, the ethereal liquid being dried and the solvent removed, when a small amount of an oily acid was obtained. This was converted into a silver salt, and the latter analyzed.

0.1280 of salt gave on ignition 0.0560 Ag. Ag = 43.7.

$C_8H_{15}O_2Ag$ requires Ag = 43.0 per cent.

Although the figures thus obtained are in fairly close agreement with those required for the silver salt of an octoic acid, it is possible that the oily acid was a mixture.

The distillate, after extraction with ether, was found to contain small amounts of formic and butyric acids.

After the removal of the volatile acids by distillation, as above described, the contents of the distillation flask were extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A small amount (about 2 grams) of an oily product was thus obtained, which became partially solid. By converting this product into a lead salt, and treating the latter with ether, an approximate separation of the acids was effected. The portion of lead salt which was soluble in ether yielded, after treatment with sulphuric acid, 0.6 gram of a dark orange-colored oil. This was unsaturated, and a determination of its iodine value gave the following result:

0.5328 absorbed 0.7601 iodine. Iodine value = 142.6.

$C_{18}H_{34}O_2$, with one ethylenic linking, requires I = 90.0 per cent.

$C_{18}H_{32}O_2$, with two ethylenic linkings, requires I = 181.4 per cent.

The oily acid therefore appears to have consisted largely of linolic acid.

The portion of lead salt which was insoluble in ether yielded 1.2 grams of solid acid, which distilled at 220–230°/15 mm., and, after recrystallization from glacial acetic acid and ethyl acetate, melted at 62°. This evidently consisted of palmitic acid.

Unsaponifiable Constituents of the Petroleum Extract.

Isolation of a Phytosterol, $C_{27}H_{46}O$, and Cetyl Alcohol.

As noted above, the portion of the petroleum extract which was insoluble in a solution of sodium carbonate and sodium hydroxide was hydrolyzed, the product acidified, extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. After this treatment the ethereal liquid was washed, dried, and the solvent removed, when an oily product was obtained which solidified on cooling. This was dissolved in alcohol, and the solution concentrated, when, after standing for some time, a quantity of a substance was deposited in the form of large, colorless plates. After recrystallization from a mixture of ethyl acetate and dilute alcohol, it separated in flattened needles, which melted at 134–135°.

0.1148 of the air-dried substance, when heated at 110°, lost 0.0054 H_2O.
H_2O = 4.7.
0.1094 of anhydrous substance gave 0.3360 CO_2 and 0.1180 H_2O.
C = 83.8; H = 12.0.
$C_{27}H_{46}O$, H_2O requires H_2O = 4.5 per cent
$C_{27}H_{46}O$ requires C = 83.9; H = 11.9 per cent.

The substance thus agrees in composition with a phytosterol, and it gave the color reactions yielded by this class of substances.

The optical rotatory power of the phytosterol was determined with the following result:

0.1349 of anhydrous substance, dissolved in 25 cc. of chloroform, gave in a 2 dcm. tube a_D —0°21′, whence $[\alpha]_D$ - 32.4°.

A small amount of the phytosterol was converted into its acetate, which separated from its solution in acetic anhydride in leaflets, melting at 119–120°.

The mother liquor from the phytosterol was evaporated, and the residue distilled under 15 mm. pressure, when the following fractions were eventually obtained: (I) Below 180°; (II) 180–190°; (III) 190–200°; (IV) 200–225°; (V) 225–250°; (VI) 250–300°; (VII) 300–320°/15 mm. The first four of these fractions contained a crystalline solid. This was collected and recrystallized several times, first from light petroleum and then from ethyl acetate. It was thus obtained in small leaflets, melting at 50–51°, and was analyzed.

0.1114 gave 0.3230 CO_2 and 0.1434 H_2O. C = 79.1; H = 14.3.
$C_{16}H_{34}O$ requires C = 79.3; H = 14.1 per cent.

This substance was thus identified as cetyl alcohol.

The above-mentioned fractions (V) and (VI) were of an oily nature, and yielded nothing definite, whereas fraction (VII), on standing for a long time, deposited a small amount of a crystalline substance. This was separated, and recrystallized from ethyl acetate, when it formed glistening leaflets, melting at 56–57°. It yielded color reactions similar to those given by the phytosterols. After further crystallization from ethyl acetate, and finally from absolute alcohol, its melting point and properties remained unchanged. The substance was then analyzed.

0.0986 gave 0.2906 CO_2 and 0.1230 H_2O. C = 80.4; H = 13.9.
$C_{18}H_{36}O$ requires C = 80.6; H = 13.4 per cent.

The composition of this substance is thus seen to agree with the formula $C_{18}H_{36}O$, and, as it differs in its properties from any substance of this formula which has hitherto been described, it would appear to be a new compound. The amount of substance, however, was too small to admit of this conclusion being confirmed.

The liquid portion of fraction (VII), from which the above-described solid had been separated, was stirred with slightly diluted alcohol, when it deposited a further quantity of phytosterol, identical with that previously obtained.

II. *Ether Extract of the Resin.*

This extract, after the removal of the solvent, was a very dark colored, soft solid. The amount employed for its investigation was about 200 grams.

Isolation of a New, Dihydric Alcohol, Ipurganol, $C_{21}H_{32}O_2(OH)_2$.

During the process of extracting the resin with ether it was observed that a small amount of a solid substance was deposited from the ethereal liquid. This was collected, and purified by extracting it in a small Soxhlet apparatus with absolute alcohol, when it was obtained perfectly white. It was subsequently crystallized from dilute pyridine, when it separated in clusters of very small needles, melting at 222–225°. The amount of this substance obtained from 200 grams of the ether extract was about 4.5 grams. On analysis it gave the following result:

0.1047 gave 0.2752 CO_2 and 0.0946 H_2O. C = 71.7; H = 10.0.
$C_{21}H_{34}O_4$ requires C = 72.0; H = 9.7 per cent.

This substance would thus appear to possess the formula $C_{21}H_{34}O_4$, and, so far as known to us, no substance of this formula has hitherto been described. It is therefore to be regarded as a new compound, and, with reference to the source from which it has been obtained and its alcoholic nature, it is proposed to designate it *ipurganol.*

The optical rotatory power of ipurganol was determined with the following result:

0.1760 of substance, dissolved in 25 cc. of pyridine, gave in a 2 dcm. tube, α_D—0.6333°, whence $[\alpha]_D$ —44.9°.

A portion of ipurganol was heated with acetic anhydride for about 2 hours, when, on cooling, a crystalline product was obtained. This was recrystallized from ethyl acetate, from which it separated in fine, colorless needles, melting at 166–167°.

0.0898 gave 0.2268 CO_2 and 0.0714 H_2O. C = 68.9; H = 8.8.
$C_{21}H_{32}O_4(CH_3.CO)_2$ requires C = 69.1; H = 8.7 per cent.

This substance is thus seen to be *diacetylipurganol*, and affords evidence of the presence in ipurganol of two hydroxyl groups.

The optical rotatory power of diacetylipurganol was determined with the following result:

0.3132 of substance, dissolved in 25 cc. of pyridine, gave in a 2 dcm. tube α_D —0.902°, whence $[\alpha]_D$ —36.0°.

An attempt to prepare a methyl derivative of ipurganol was not successful.

Ipurganol yields color reactions which are similar to those given by the phytosterols. Thus, if the substance be dissolved in chloroform with a little acetic anhydride, and a drop of concentrated sulphuric acid subsequently added, a purplish pink coloration is first produced, which changes to blue, then to bright green, and finally becomes brown.

If concentrated sulphuric acid be added to ipurganol, the latter is colored deep reddish brown, while the acid soon acquires a yellow color with a green fluorescence.

In connection with the above description of ipurganol, it may be noted that it appears to be closely related to two substances of alcoholic nature which have quite recently been isolated in these laboratories. One of these was obtained from the resin of *Grindelia camporum*, Greene,[1] and agrees in composition with the formula $C_{28}H_{38}O_4$. It melts at 256–257°, and yields an acetyl derivative melting at 161°. This compound, which was not previously named, may now conveniently be designated as *grindelol*. The other substance was obtained from the resin of watermelon seeds, and has been designated *cucurbitol*. It possesses the formula $C_{24}H_{40}O_4$, melts at 260°, and yields an acetyl derivative melting at 150°. The three substances show slight differences in their color reactions when subjected to the above-mentioned test in chloroform solution with acetic anhydride and concentrated sulphuric acid. Thus grindelol and cucurbitol give at first a blue color, changing to dull green, and finally becoming brown, the intermediate greenish tint being less pronounced in the case of the last-mentioned substance. In view of the composition and character of these three new compounds, it is evident that they are members of a homologous series, which is represented by the general formula $C_nH_{2n-8}O_4$.

Treatment of the Ether Extract with Alkalis.

I. *Extraction with Ammonium and Sodium Carbonates.*—The ethereal solution of the ether extract, from which the ipurganol had been removed, as above described, was successively extracted with solutions of ammonium carbonate and sodium carbonate. This treatment, however, removed only small amounts of black resin. The ethereal liquid was then shaken with several successive portions of water, which removed a quantity of the sodium compound of a resin. These aqueous liquids were united and acidified, when the resin was precipitated, after which it was extracted with ether, the ethereal liquid being dried and the solvent removed. The large quantity (70 grams) of resinous material thus obtained was dissolved in alcohol, treated with animal charcoal, and the filtered liquid concentrated and allowed to stand for some time. As nothing could be separated by this means, the small amount of resin which had previously been extracted by sodium carbonate and treated in the same manner as the last-mentioned product was added to the alcoholic solution of the latter, together with such an amount of sulphuric acid as to represent about 5 per cent. of the mixture. The whole was then heated in a reflux apparatus for about 6 hours, after which water was added and the alcohol removed. The aqueous, acid liquid, from which a quantity of a soft resin had separated, was subsequently distilled with steam until volatile products ceased to pass over. The distillate, which contained some yellow, oily drops, was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. This alkaline, aqueous liquid was acidified, extracted with ether, and the solvent removed, when a small amount (0.4 gram) of an oily acid was obtained. The latter was converted into an ammonium salt, from which by precipitation with silver nitrate two fractions of a silver salt were prepared, and these were analyzed.

---

[1] *Proc. Am. Pharm. Assoc.*, 55, 342 (1907).

I. 0.2138 of salt gave on ignition 0.0734 Ag. Ag = 34.3
II. 0.1060 of salt gave on ignition 0.0410 Ag. Ag = 38.7
$C_{12}H_{23}O_2Ag$ requires Ag = 35.2 per cent.; $C_{10}H_{19}O_2$ Ag requires Ag = 38.7 per cent.

The ethereal liquid which had been shaken with sodium carbonate was dried, and the solvent removed, when a small quantity (1.5 grams) of a neutral, oily liquid was obtained. This was distilled under diminished pressure, when it passed over between 90 and 160°/15 mm. It gave no coloration with ferric chloride, but responded to the test for furfural.

The above-mentioned distillate, after extraction with ether, was found to contain small amounts of formic and butyric acids.

After the removal of the volatile products of hydrolysis by distillation with steam, as above described, there remained in the distillation flask a reddish-colored, aqueous liquid, and a soft, resinous mass which floated on the surface. The whole was shaken with ether, when the resinous material became completely dissolved. On subsequently extracting the ethereal liquid with sodium carbonate, about 3 grams of amorphous, dark colored resin were removed. The ethereal liquid was then dried, and the solvent evaporated, when 2 grams of a dark reddish-colored oil were obtained, which distilled between 210 and 250° under 15 mm. pressure. This oil separated no solid on standing. It gave a greenish yellow color with ferric chloride, and absorbed bromine in chloroform solution, but no definite product could be obtained from it.

The aqueous liquid which remained in the distillation flask after the removal of the volatile products of hydrolysis, and from which the soft, resinous mass had been separated, was treated with baryta for the removal of the sulphuric acid, and filtered. It then reduced Fehling's solution, but an attempt to prepare an osazone from it was not successful.

II. *Extraction with Sodium Hydroxide.*—After the treatment of the ethereal solution of the ether extract with ammonium and sodium carbonates it was shaken with two successive portions of a 10 per cent. solution of sodium hydroxide, and finally washed with water. The liquids thus obtained, which were dark in color, were acidified and extracted with ether, when it was observed that a small amount of a solid substance was deposited. This was found to consist of ipurganol, for, when treated with acetic anhydride, it yielded diacetylipurganol, melting at 166–167°. On subsequently evaporating the ethereal liquid a quantity (50 grams) of dark colored, resinous material was obtained, which possessed a somewhat disagreeable odor. As nothing could be separated from this resin, it was dissolved in alcohol, and a little water added, together with such an amount of sulphuric acid as to represent about 5 per cent. of its weight. The mixture was then heated in a reflux apparatus for 4 hours, after which water was added, the alcohol evaporated, and steam passed through the mixture until all the volatile products had been removed. The distillate, which contained some oily drops floating on the surface, was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. This alkaline, aqueous liquid was acidified, extracted with ether, and the solvent removed, when a small quantity of an oily acid was obtained. The latter was converted into an ammonium salt, from which a silver salt was prepared and analyzed.

0.2954 of salt gave on ignition 0.1026 Ag. Ag = 34.7
0.0658 of salt gave on ignition 0.0224 Ag. Ag = 34.0
$C_{12}H_{23}O_2$ Ag requires Ag = 35.2 per cent.

The ethereal liquid which had been shaken with sodium carbonate was dried, and the solvent removed, when a small quantity (about 3.5 grams) of a neutral yellowish oil was obtained. This was distilled under diminished pressure, when it passed over between 90 and 180°/20 mm., and was evidently a complex mixture.

The above-mentioned distillate, after extraction with ether, was found to contain small amounts of formic and butyric acids.

After the removal of the volatile products of hydrolysis, as above described, there remained in the distillation flask an aqueous, acid liquid, together with a cake of solid substance. The whole was shaken with ether, when the solid substance became completely dissolved. The ethereal liquid was extracted with sodium carbonate, which removed a quantity of soft, resinous material, after which it was dried, and the solvent removed. A quantity of a light colored oil was thus obtained, which solidified on cooling, and when distilled under diminished pressure passed over for the most part between 200 and 210°/25 mm. In order to ascertain its character, it was heated for a short time with an alcoholic solution of potassium hydroxide, and the liquid poured into water, when about 2 grams of a solid substance separated. This was extracted with ether, the ethereal liquid being dried and the solvent removed, when a residue was obtained which, after several crystallizations from light petroleum, melted at 49–50°.

0.1592 gave 0.4614 CO_2 and 0.2024 H_2O. C = 79.0; H = 14.1.
$C_{16}H_{34}O$ requires C = 79.3; H = 14.1 per cent.

This substance was thus identified as cetyl alcohol, which had also been obtained from the petroleum extract of the resin.

The aqueous liquid which remained in the distillation flask after the removal of the volatile products of hydrolysis, and which had been extracted with ether, was subsequently treated with baryta for the removal of the sulphuric acid. The filtered liquid, when concentrated, yielded a very small amount of a sirup, but this did not reduce Fehling's solution, and therefore contained no sugar.

The ethereal solution of the original ether extract, after being treated with alkalis, as above described, was dried, and the solvent removed. About 10 grams of a light-colored, viscid product were thus obtained, from which a very small amount of a phytosterol was separated.

III. Chloroform Extract of the Resin.

This extract, after the removal of the solvent, was a hard, dark reddish brown mass, which could be reduced to a light brown powder. The amount employed for its investigation was about 350 grams.

Treatment with Sodium Carbonate.

Isolation of β-Methylaesculetin, $C_9H_5(CH_3)O_4$.

As the solution of the extract in chloroform deposited nothing on standing, it was shaken with a solution of sodium carbonate, when a large quantity of a thick, dark brown, tarry product was formed, consisting of the sodium compound of an acidic resin. The chloroform liquid had then become nearly deprived of color, and was found to contain only a small amount of resinous material, while the aqueous, alkaline liquid was dark in color and showed a marked blue fluorescence.

The above-mentioned, tarry product was washed several times with a solution of sodium carbonate. These washings, together with the sodium carbonate extract first obtained, were acidified, when a small quantity of an amorphous, brown solid separated, which was removed by filtration. The acid filtrate was extracted with ether, the ethereal liquid being dried, and the solvent removed, when a small quantity of a sirup was obtained which, after long standing, deposited a crystalline substance. This was collected, and recrystallized from ethyl acetate, from which it separated in nearly colorless needles, melting at 200–202°. The solution of this substance, on the addition of a little ammonia, displayed a fine blue fluorescence. As the amount was too small for analysis, it was heated with acetic anhydride, when it yielded an acetyl derivative melting at 176°. This melting point remained unchanged when the acetylated substance was mixed with acetyl-β-methylaesculetin prepared from the respective compound isolated from the bark of *Prunus serotina.*[1] The identity of the above-described, crystalline substance (m. p. 200–202°) with β-methylaesculetin was therefore definitely established.

Treatment of the Sodium Compound of the Resin with Dilute Alcoholic Sulphuric Acid.

The large quantity of thick, dark brown, tarry product above referred to was dissolved in alcohol, a slight excess of sulphuric acid added, and the mixture poured into water. The liberated resin was then taken up with chloroform, and the solvent removed, after which it was dissolved in alcohol. To this solution some water was added, and such an amount of sulphuric acid that the latter represented about 5 per cent. of the weight of the mixture. This was subsequently boiled in a reflux apparatus for about 12 hours, after which water was added, the alcohol removed, and the mixture distilled with steam until volatile products ceased to pass over. The distillate, which contained some oil floating on the surface, was completely extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate, after which it was dried and the solvent removed. A neutral, oily product was thus obtained, but it was found to be a mixture, and the amount was too small for its further examination.

The above-mentioned sodium carbonate extract of the volatile product was acidified and extracted with ether, the ethereal liquid being dried and the solvent removed, when 1.5 grams of an oily acid were obtained. This distilled for the most part between 174 and 178° under the ordinary pressure, and was analyzed.

0.1258 gave 0.2702 CO_2 and 0.1128 H_2O. C = 58.6; H = 10.0.
$C_5H_{10}O_2$ requires C = 58.8, H = 9.8 per cent.

This acid was dextrorotatory, and was thus identified as *d*-methylethylacetic acid, which is stated to boil at 175°.

The remainder of this liquid, together with a portion of somewhat higher boiling point, was converted into a silver salt. This was obtained in two fractions, both of which were analyzed.

I. 0.3256 of salt gave on ignition 0.1678 Ag. Ag = 51.5
II. 0.4332 of salt gave on ignition 0.2244 Ag. Ag = 51.8
$C_5H_9O_2Ag$ requires Ag = 51.7 per cent.

The above-mentioned aqueous distillate, after extraction with ether, was found to contain small amounts of formic and butyric acids.

After the removal of the volatile products of the acid hydrolysis by distillation with steam, as above described, there remained in the distillation flask an acid liquid, together with a soft, resinous mass. The liquid was decanted from the resin and extracted with ether, which, however, removed only a small amount of an oily product. It was then treated with baryta for the removal of the sulphuric acid, filtered, and concentrated. A sirup was thus obtained, which readily yielded *d*-phenylglucosazone, melting at 210–211°. It was therefore evident that at least a portion of the chloroform extract of jalap resin was glucosidic.

---

[1] *J. Chem. Soc.*, 95, 256 (1909).

The previously mentioned, soft, resinous mass, which had been separated from the acid, aqueous liquid, as above described, was treated with hot ether, in which the greater portion was soluble. The ethereal solution was separated from the insoluble material, consisting of a black, hard resin, and extracted with a solution of sodium carbonate, after which it was dried, and the solvent removed. About 5 grams of a sirupy product were thus obtained, which was distilled under diminished pressure, when it passed over quite constantly at 210–211° as a lemon-yellow oil. This oil solidified on cooling to a white, crystalline mass, which was first dried on a porous plate and finally in a desiccator, when it melted at 23–25°.

0.0850 gave 0.2204 CO_2 and 0.0926 H_2O. C = 70.7; H = 12.1.
$C_{17}H_{34}O_3$ requires C = 71.3; H = 11.9 per cent.

This substance was evidently the *ethyl ester of convolvulinolic acid*, $C_{15}H_{29}O_3.C_2H_5$, and its formation during the treatment of the acidic portion of the chloroform extract with alcoholic sulphuric acid may be attributed to the amount of water present not having been sufficient to entirely prevent esterification. It agrees in character with the ethyl convolvulinolate prepared by Hoehnel,[1] which is stated to melt at 22.5°.

The sodium carbonate extract of the ethereal liquid from which the ethyl convolvulinolate was obtained was acidified and extracted with ether, the ethereal liquid being dried and the solvent removed, when it yielded a quantity of a dark colored sirup, which became partially solid on standing. This sirup was dissolved in alcohol, brought onto purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum and ether.

Petroleum Extract:—This was a dark, orange colored sirup, which solidified to a soft, fat-like mass. It was distilled under diminished pressure, and the following fractions collected: (I) Below 220°; (II) 200–225°; (III) 225–230°; (IV) 230–290/15 mm. As no crystalline acid could be obtained from these fractions, they were converted into silver salts, and the latter analyzed.

From these results it is evident that the above-described petroleum extract was a mixture. It undoubtedly contained some convolvulinolic acid, $C_{15}H_{30}O_3$, and apparently also a higher homologue of the latter.

---

[1] *Arch. Pharm.*, 234, 677 (1896).

Fraction I.	0.3474 of salt gave on ignition 0.1124 Ag.	Ag = 32.4
Fraction II (a).	0.2032 of salt gave on ignition 0.0572 Ag.	Ag = 28.1
Fraction II (b).	0.2094 of salt gave on ignition 0.0594 Ag.	Ag = 28.4
Fraction III (a).	0.2780 of salt gave on ignition 0.0752 Ag.	Ag = 27.0
Fraction III (b).	0.3588 of salt gave on ignition 0.0978 Ag.	Ag = 27.3
Fraction III (c).	0.3017 of salt gave on ignition 0.0830 Ag.	Ag = 27.5
Fraction IV.	0.2442 of salt gave on ignition 0.0648 Ag.	Ag = 26.5

$C_{15}H_{20}O_8$ Ag requires Ag = 29.6 per cent.
$C_{17}H_{22}O_8$ Ag requires Ag = 27.5 per cent.

Ether Extract.—This was a dark red sirup. It was distilled under diminished pressure, when some decomposition occurred, and, although a portion of the distillate became solid, nothing definite could be isolated from it.

IV. *Ethyl Acetate Extract of the Resin.*

This extract, after the removal of the solvent, was a hard, friable, reddish brown mass, which could easily be reduced to a light brown powder.

Treatment with Dilute Alcoholic Sulphuric Acid.

One hundred grams of the dry extract were dissolved in alcohol, and some water added, together with such an amount of sulphuric acid that the latter represented about 5 per cent. of the weight of the mixture. The liquid, which amounted to 1.5 liters, was then heated in a reflux apparatus for about 5 hours, after which the alcohol was removed, water added, and steam passed through the mixture until volatile products ceased to pass over. The distillate, which contained some oily drops floating on the surface, was extracted with ether. The ethereal liquid was shaken with a solution of sodium carbonate, after which it was washed, dried, and the solvent removed. A very small amount of a yellowish oil was thus obtained, which gave a reaction for furfural. The sodium carbonate extract, when acidified and extracted with ether, yielded about 2 grams of a dark yellow, oily acid. This was distilled under the ordinary pressure, when it passed over for the most part between 174 and 178°.

0.1710 gave 0.3682 CO_2 and 0.1494 H_2O. C = 58.7; H = 9.7.
$C_5H_{10}O_2$ requires C = 58.8; H = 9.8 per cent.

An alcoholic solution of this acid was dextrorotatory, which confirmed its identity as *d*-methylethylacetic acid.

The above-mentioned, aqueous distillate, after extraction with ether, was found to contain formic and butyric acids.

After the removal of the volatile products of hydrolysis by distillation with steam, as above described, there remained in the distillation flask a dark red liquid, and a quantity of soft, resinous material which floated on the surface. The aqueous, acid liquid was separated from the resin, and extracted with ether, but this removed only a small amount of an oily product. It was finally treated with baryta from the removal of the sulphuric acid, filtered, and concentrated. A considerable quantity of a sirup was thus obtained, which readily yielded *d*-phenylglucosazone, melting at 206–207°. It was thus evident that at least a portion of the ethyl acetate extract of the resin was glucosidic.

The previously mentioned soft, resinous material, which had been separated from the above described, aqueous, acid liquid, was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum and ether.

Petroleum Extract.—This was a dark orange-colored sirup, which became partially solid on standing, and amounted to 10 grams. It was dissolved in ether, and the ethereal liquid shaken with a solution of sodium carbonate, after which the ether was dried and evaporated, when 2 grams of a dark yellow, oily liquid were obtained. The sodium carbonate extract was acidified and extracted with ether, the ethereal liquid being dried and the solvent removed. A quantity (4.7 grams) of an oily acid was thus obtained, which became solid on standing. The above-mentioned 2 grams of yellow, oily liquid were found to consist of an ester which had been formed by the treatment of the resinous material with alcoholic sulphuric acid. This was therefore hydrolyzed, and the acid thus obtained mixed with the 4.7 grams of acid previously obtained by extraction with sodium carbonate. The whole was then distilled under diminished pressure, when the greater portion passed over between 210 and 230°/12 mm., and formed a light yellow, soft solid. This was neutralized with potassium hydroxide, when a portion of the resulting potassium salt was observed to be sparingly soluble. The acid obtained from this sparingly soluble salt was dissolved in a mixture of light petroleum and ether, from which it separated in the form of a nearly colorless solid, melting at 47–48°.

0.1104 gave 0.2810 CO_2 and 0.1196 H_2O. C = 69.4; H = 12.0.
$C_{15}H_{30}O_3$ requires C = 69.8; H = 11.6 per cent.

This substance was thus identified as convolvulinolic acid, a further quantity of which was obtained from the alcohol extract of the resin.

The acid obtained from the more soluble portion of the above-described potassium salt was a soft, fat-like mass. From a portion of it three fractions of silver salt were prepared and analyzed.

I. 0.3118 of salt gave on ignition 0.0868 Ag. Ag = 27.8
II. 0.3014 of salt gave on ignition 0.0842 Ag. Ag = 27.9
III. 0.0626 of salt gave on ignition 0.0184 Ag. Ag = 29.4

$C_{16}H_{31}O_2$ Ag requires Ag = 29.6 per cent.
$C_{18}H_{35}O_2$ Ag requires Ag = 27.5 per cent.

These results would indicate that the above-described product consisted chiefly of a higher homologue of convolvulinolic acid, having the formula $C_{17}H_{34}O_3$. As previously noted, a similar product was obtained by the acid hydrolysis of the chloroform extract.

Ether Extract.—This was a soft, black, resinous mass, and amounted to 8 grams. It was examined, but nothing of a definite character could be obtained from it.

V. *Alcohol Extract of the Resin.*

This extract, as indicated in the first part of this paper, was the chief constituent of the original crude resin. When quite dry it could readily be reduced to a light brown powder, and on treating it in dilute alcoholic solution with successive portions of animal charcoal, a nearly white product was obtained. The latter, after drying at 110°, melted at 150–160°, and, when heated on platinum foil, it burned with a smoky flame, leaving no residue.

The optical rotatory power of the purified alcohol extract was determined, with the following result:

A solution containing 0.9905 gram of dry substance in 25 cc. of absolute alcohol had α_D —1.47° in a 1 dcm. tube, whence $[\alpha]_D$ —37.1°.

This value is almost precisely the same as that obtained for the purified total resin, namely $[\alpha]_D$ —37.0°, as recorded in the first part of the paper. It also agrees closely with the rotation ($[\alpha]_D$ —36.9°) observed by Kromer[1] for the product designated as "convolvulin," the latter consisting of that portion of jalap resin which is insoluble in ether.

Fusion with Potassium Hydroxide.

Twenty grams of the alcohol extract of the resin were fused with 120 grams of potassium hydroxide in a nickel basin, the temperature of the mixture being kept at about 150° for some time, after which it was slowly increased to 260°, with constant stirring. When the reaction had ceased, and the mass had become pasty, it was allowed to cool, and then dissolved in water. The solution was acidified with sulphuric acid, and distilled with steam until volatile products ceased to pass over. The distillate, which was found to contain only acidic substances, was made alkaline with sodium carbonate, the liquid concentrated, acidified, and extracted with ether, when a quantity of an oily acid was obtained. This was distilled twice under the ordinary pressure, and the following fractions finally collected: (1) Below 165°; (2) 165–175°; (3) 175–185°; (4) 185–245°; (5) 245–280°. Fractions (1), (2) and (3) were analyzed.

It would appear from these results that fraction (1) consisted of a nearly pure butyric acid, while fractions (2) and (3) evidently contained valeric acid. The subsequent fractions consisted of mixtures of acids of higher molecular weight.

---

[1] *J. Chem. Soc. Abst.*, 66, i, 540 (1894).

(1) 0.1940 gave 0.3870 CO_2 and 0.1586 H_2O. C = 54.4; H = 9.1
(2) 0.1732 gave 0.3660 CO_2 and 0.1478 H_2O. C = 57.6; H = 9.5
(3) 0.1862 gave 0.4124 CO_2 and 0.1652 H_2O. C = 60.4; H = 9.9
$C_4H_8O_2$ requires C = 54.5; H = 9.1 per cent.
$C_5H_{10}O_2$ requires C = 54.8; H = 9.8 per cent.
$C_6H_{12}O_2$ requires C = 62.1; H = 10.3 per cent.

The aqueous liquid from which the above-mentioned acids had been extracted by ether was distilled with steam, when the distillate was found to contain formic, acetic, and butyric acids.

After the removal of the volatile products of the potash fusion by distillation with steam, there remained in the distillation flask a yellow, aqueous liquid, which was completely extracted with ether. The ethereal liquid was washed, dried, and the solvent removed. A sirupy liquid was thus obtained, which, after standing for a few days, solidified to a crystalline mass. This was dissolved in water, the solution treated with animal charcoal and concentrated, when a product was obtained which, after further crystallization from water, separated in long, flat needles, melting at 110–111°. As the amount of this acid was small, it was converted into a silver salt, and the latter analyzed.

0.1918 of salt gave on ignition 0.1000 Ag. Ag = 52.1.
$C_{10}H_{16}O_4Ag_2$ requires Ag = 51.9 per cent.

The above-described substance was thus identified as sebacic acid, $C_{10}H_{18}O_4$, and its low melting point was evidently due to a slight impurity. This acid, as will be noted later, had been obtained by Hoehnel by the oxidation of convolvulinolic acid, $C_{14}H_{28}(OH)CO_2H$, but was regarded by him as an isomeride of sebacic acid, and therefore designated "ipomic acid."[1]

The mother liquor from the first crystallization of the sebacic acid was concentrated to a small bulk, when an acid separated in the form of laminae, which, after further crystallization, melted at 103–104°.

0.1082 gave 0.2274 CO_2 and 0.0862 H_2O. C = 57.3; H = 8.8.
$C_9H_{16}O_4$ requires C = 57.4; H = 8.5 per cent.

This substance was thus identified as azelaic acid, which had previously been obtained by the authors in a similar manner from the alcohol extract of the resin of *Ipomoea purpurea*, Roth.[2]

Hydrolysis of the Alcohol Extract of the Resin with Barium Hydroxide.

A quantity (200 grams) of the purified alcohol extract was dissolved in alcohol (1000 cc.), and a cold, saturated solution of barium hydroxide gradually added until the liquid showed an alkaline reaction. The liquid was then kept at a temperature of 35–40°, small portions of solution of barium hydroxide being added from time to time in order to maintain alkalinity. This treatment was continued until, on testing a small portion of the liquid with water, no turbidity was produced, a condition which was obtained in about 12 hours. The liquid was then allowed to cool, a little water added, and the alcohol removed, after which it was deprived of the excess of barium by means of carbon dioxide and filtering. The barium, which still remained in the filtrate in combination with the acids formed from the resin, was exactly precipitated with sulphuric acid, when, after removing the barium sulphate, a clear, dark red liquid was obtained. This liquid was subjected to distillation with steam in order to remove any volatile acids present. The distillate, which contained some oily drops floating on the surface, was made alkaline with sodium carbonate, concentrated, then acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A quantity (4 grams) of an oily product was thus obtained, which had the odor of valeric acid, and distilled between 174 and 176° as a colorless liquid.

---

[1] *Arch. Pharm.*, 234, 680 (1896).

[2] *Amer. J. Pharm.*, 80, 271 (1908).

0.1678 gave 0.3614 CO_2 and 0.1524 H_2O. C = 58.7; H = 10.1.
$C_5H_{10}O_2$ requires C = 58.8; H = 9.8 per cent.

The density of the acid was 0.9480 at 16.5°. It was optically active, and a determination of its specific rotatory power gave the following result:

α_D in a 25 mm. tube at 16° = +4° 10′, whence $[\alpha]_D$ +17.58°.

It was thus evident that the above-described liquid consisted of the optically active valeric acid (*d*-methylethylacetic acid, $CH(CH_3)(C_2H_5).CO_2H$), which is recorded[1] as having $[\alpha]_D$ +17.85°.

The liquid from which the valeric acid had been removed by extraction with ether was distilled with steam, when the distillate was found to contain small amounts of formic and butyric acids.

After the removal of the total volatile acids by distillation with steam, as above described, there remained in the distillation flask a clear liquid. This was extracted with ether, which, however, removed nothing. It was then concentrated under diminished pressure to the consistency of a sirup, when it still remained clear, and possessed a dark orange-yellow color. It had a strongly acid reaction, and did not reduce Fehling's solution until after heating with a mineral acid. For the further examination of this product, which may be termed the *hydrolyzed resin*, it was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with the same solvents as had been employed for the extraction of the original mixture of resins. The results were as follows:

Petroleum (b. p. 40–60°) removed nothing.

---

[1] *Ber.*, 29, 52 (1896).

Ether and chloroform extracted 19.3 grams and 9 grams respectively of clear, orange-yellow sirups, which did not solidify.

Ethyl acetate extracted 54 grams of a dark, opaque sirup, which, when perfectly dry, could be reduced to a light brown powder. The latter was extremely hygroscopic, but if kept in a sealed tube, could be preserved unchanged.

Alcohol extracted 88 grams of a product, which formed a hard, brittle mass, and could be reduced to a nearly colorless powder.

Each of the above products from the hydrolyzed alcohol extract of the resin was then subjected to treatment with dilute sulphuric acid.

Ether Extract of the Hydrolyzed Resin.

The entire amount of this extract (19 3 grams) was dissolved in water, and such an amount of sulphuric acid added that the latter represented 5 per cent. by weight of the solution. The whole was then boiled in a reflux apparatus for about 6 hours, when a sirupy product separated which did not become solid on cooling, and the mixture was subsequently distilled with steam. The distillate, which contained a light yellow oil floating on the surface, was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. On evaporating the ether a very small amount of a neutral oil was obtained, which did not respond to the test for furfural and gave no color with ferric chloride. The sodium carbonate liquid was acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when 1.2 grams of a light yellow oil were obtained. This was unsaturated, since it absorbed bromine. It was distilled under diminished pressure, when the following two fractions were collected: (I) 120–140°; (II) 140–160°/15 mm., the latter distilling for the most part at about 160°/15 mm. The first fraction was analyzed with the following result:

I. 0.1480 gave 0.3534 CO_2 and 0.1362 H_2O. C = 65.1; H = 10.2.
$C_7H_{12}O_2$ requires C = 65.6; H = 9.4 per cent.

The remaining portion of this liquid yielded a fraction of silver salt which gave the following result on analysis:

0.1494 gave 0.2342 CO_2, 0.0796 H_2O, and 0.0590 Ag. C=42.7; H=5.9; Ag =39.5.
$C_{10}H_{17}O_2$ Ag requires C = 43.3; H = 6.1; Ag = 39.0 per cent.

Fraction I thus apparently consisted of a mixture of an acid $C_{10}H_{18}O_2$ with one of lower molecular weight.

II. 0.1560 gave 0.3978 CO_2 and 0.1516 H_2O. C = 69.5; H = 10.8.
$C_{10}H_{18}O_2$ requires C = 70.6; H = 10.6 per cent.

From the remainder of this fraction a silver salt was prepared and analyzed.

0.1270 gave 0.2000 CO_2, 0.0746 H_2O, and 0.0492 Ag. C=43.0; H=6.5; Ag=38.7.
$C_{10}H_{17}O_2$ Ag requires C = 43.3; H = 6.1; Ag = 39.0 per cent.

It will be seen from these results that fraction II agrees approximately in composition with a decylenic acid, $C_{10}H_{18}O_2$, but the amount of material available did not permit of its more complete examination. It was therefore impossible to ascertain whether the product was homogeneous.

Hoehnel,[1] by the treatment of so-called "purgic acid" with dilute sulphuric acid, obtained a product (b. p. 176°/135 mm.) which he regarded as decylenic acid, but this conclusion was based only upon the analysis of two amorphous salts and a determination of the iodine value. The latter figure, as found by Hoehnel (82.5), is, moreover, not in agreement with that required for decylenic acid, which is 146. It therefore cannot be considered as definitely established that decylenic acid has been obtained from jalap resin.

The aqueous distillate from which the oily acid had been obtained by extraction with ether was found to contain, furthermore, small amounts of formic and butyric acids.

After the removal of the volatile products by distillation with steam, as above described, there remained in the distillation flask a yellowish liquid, together with a viscid, oily product which floated on the surface. The mixture was extracted with ether, in which the oily product was completely soluble, and the ethereal solution then shaken with a solution of sodium carbonate. On subsequently evaporating the ether, only a very small amount of a neutral, oily liquid was obtained. The sodium carbonate liquid was acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when a quantity of a viscid, dark orange-colored product was obtained, which deposited nothing crystalline. When neutralized with a solution of sodium hydroxide, it formed a gelatinous mass, having the character of a soap The viscid, oily acid was distilled under diminished pressure, and the following fractions collected: (I) 192–194°; (II) 194–200°; (III) 200–210°; (IV) 210–220°; (V) 220–280°; (VI) 280–310°/15 mm. The total amount of these fractions was 12.2 grams. They were all viscid, yellow, unsaturated liquids, and on analysis gave the following results:

I 0.1492 gave 0.3520 CO_2 and 0.1398 H_2O. C = 64.3; H = 10.4
II. 0.1372 gave 0.3236 CO_2 and 0.1336 H_2O. C = 64.3; H = 10.8
III. 0.1778 gave 0.4202 CO_2 and 0.1714 H_2O. C = 64.5; H = 10.7
IV. 0.1152 gave 0.2770 CO_2 and 0.1126 H_2O. C = 65.7; H = 10.9
V. 0.1758 gave 0.4294 CO_2 and 0.1678 H_2O. C = 66.6; H = 10.6
VI. 0.1560 gave 0.3904 CO_2 and 0.1496 H_2O. C = 68.2; H = 10.6

The iodine absorption values of fractions I and VI were determined.

I. 0.3176 absorbed 0.0980 I. Iodine value = 30.9
VI. 0.3910 absorbed 0.1986 I. Iodine value = 50.8

---

[1] *Arch. Pharm.*, 234, 668 (1896).

It was evident from these results that the above fractions consisted of a mixture of acids, the identity of which could not be established.

The aqueous, acid liquid contained in the distillation flask, from which the above-described products had been removed by extraction with ether, was treated with baryta for the removal of the sulphuric acid. The filtered liquid was then concentrated under diminished pressure, when a small amount of a sirup was obtained which contained sugar, since it readily yielded *d*-phenylglucosazone, melting at 209–210°. This sirup also contained a small amount of a readily soluble, organic acid.

Chloroform Extract of the Hydrolyzed Resin.

This extract, which amounted to only 9 grams, was subjected to the same treatment with dilute sulphuric acid as has been described in connection with the ether extract of the hydrolyzed resin. On distilling the product with steam, a very small amount of an oily acid was obtained, together with formic and butyric acids. The contents of the distillation flask consisted of an aqueous, acid liquid, on the surface of which there was a small amount of a dark colored, viscid oil. The mixture was extracted with ether, which completely dissolved the oily product, the ethereal liquid being then shaken with a solution of sodium carbonate. On subsequently evaporating the ether, a very small amount of a neutral oil was obtained. The sodium carbonate liquid was acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A small amount of a dark orange-colored oil was thus obtained, from which no solid substance separated. It was therefore mixed with purified sawdust, and the mixture successively extracted with light petroleum and ether, but the resulting products were of an oily nature, and did not solidify. The acids were finally converted by fractional precipitation into a number of silver salts, the analysis of which, however, indicated them to consist of complex mixtures. The above-mentioned, aqueous liquid which had been extracted with ether was finally treated with baryta for the removal of the sulphuric acid, and filtered. It was then found to contain sugar, since it readily yielded *d*-phenylglucosazone, melting at 207–208°. It also contained a readily soluble, organic acid.

Ethyl Acetate Extract of the Hydrolyzed Resin.

This extract, which amounted to 54 grams, was obtained in the form of a dark, opaque sirup. As previously noted, it could be reduced to a powder after thorough drying, but the latter was extremely hygroscopic. It was heated for about 6 hours with dilute sulphuric acid, in the same manner as the two preceding extracts, and the product distilled with steam. The distillate, which contained some oily drops, was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. On subsequently evaporating the ether, only a very small amount of a neutral, oily liquid remained. The sodium carbonate liquid was then acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A quantity (5.2 grams) of an acid was thus obtained, which was distilled under the ordinary pressure, when it passed over for the most part between 174 and 178°.

0.1792 gave 0.3842 CO_2 and 0.1570 H_2O. $C = 58.5$; $H = 9.7$.
$C_5H_{10}O_2$ requires $C = 58.8$; $H = 9.8$ per cent.

The density of the acid was 0.9388 at 17.5°. A determination of its optical rotatory power gave the following result:

α_D in a 25 mm. tube at $17.5° = +4°7,'$ whence $[\alpha]_D + 17.53°$.

This acid was thus identified as the optically active valeric acid (*d*-methylethylacetic acid), $CH(CH_3)(C_2H_5).CO_2H$.

The distillate which had been extracted with ether was found to contain small amounts of formic and butyric acids.

After the removal of the volatile products by distillation with steam there remained in the distillation flask a dark colored liquid, together with a solid cake of resin, which was separated by filtration. The clear liquid was extracted with ether, but this removed only a small amount of oily substance, which did not permit of further examination. After extraction with ether the liquid was treated with baryta for the removal of the sulphuric acid, filtered, and the filtrate concentrated under diminished pressure. A sirup was thus obtained which contained sugar, since it yielded *d*-phenylglucosazone, melting at 207–208°. It also contained an organic acid which was readily soluble in water.

The above-mentioned, solid cake of resin, which was separated from the aqueous, acid liquid, was dissolved in alcohol, mixed with purified sawdust, and the mixture successively extracted with light petroleum, ether, and alcohol. The products from the first two solvents were of an oily nature, while the alcohol removed only a small amount of a hard resin. The petroleum and ether extracts were further examined, but they appeared to consist of a complex mixture of acids, of which no constituent could be definitely identified.

Alcohol Extract of the Hydrolyzed Resin.

This constituted the largest portion of the product of the alkaline hydrolysis of the resin. It formed a hard, transparent, light yellow mass, which could be reduced to a nearly colorless powder, and, unlike the ethyl acetate extract, was permanent in the air. It dissolved readily in water, yielding a clear solution, which was strongly acid to litmus. It melted at 110–115°, and with cold, concentrated sulphuric acid gave a deep red color. It was optically active, and a determination of its specific rotatory power gave the following result:

An aqueous solution containing 1.1060 grams of substance in 25 cc. had α_D —1° 29′ in a 1 dcm. tube, whence $[\alpha]_D$ —33.53°.

Hoehnel[1] has recorded for the so-called "convolvulic acid," to which he assigned the formula $C_{45}H_{80}O_{28}$, and which represented that portion of the product of the alkaline hydrolysis of "convolvulin" which was insoluble in ether and not volatile in steam, a specific rotatory power of —34.68°; whereas Kromer[2] had noted for a somewhat similar product $[\alpha]_D$ —31.33°.

For the examination of the above-mentioned extract 100 grams of material were employed. This was dissolved in water, and such an amount of sulphuric acid added that the latter represented 5 per cent. by weight of the mixture. The whole was then heated in a reflux apparatus for 4 hours, and the mixture allowed to cool, when it was observed that a resinous product had separated in the form of a soft, plastic mass. On passing steam through the mixture a slightly acid distillate was obtained, which contained no oily drops. It was made alkaline with sodium carbonate, concentrated, then acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A very small amount of an oily acid was thus obtained, which was converted into a silver salt, and the latter analyzed.

0.1396 of salt gave on ignition 0.0728 Ag. Ag = 52.1.
$C_5H_9O_2$ Ag requires Ag = 51.7 per cent.

This acid was thus identified as a valeric acid.

The acid liquid which had been extracted with ether was distilled with steam, when the distillate was found to contain small amounts of formic and butyric acids.

After the removal of the volatile products there remained in the distillation flask a dark colored liquid, which was decanted from the mass of resinous material and extracted with ether, but this removed only a small amount of a mixture of acids. The aqueous, acid liquid was finally treated with baryta for the removal of the sulphuric acid, and the filtered liquid concentrated under diminished pressure. A sirup was thus obtained which contained sugar, since it readily yielded *d*-phenylglucosazone, melting at 209–210°. It also contained a readily soluble organic acid.

The resinous material obtained by the above treatment, and which had been separated from the aqueous, acid liquid, was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively with light petroleum, ether, and alcohol.

Petroleum Extract.—This was a light yellow oil, which solidified to a fat-like mass, and amounted to 11.2 grams.

---

[1] *Arch. Pharm.*, 234, 662 (1896).

[2] *J. Chem. Soc. Abst.*, 66, i, 540 (1894).

Ether Extract.—This product was a soft, dark brown mass, and amounted to 9 grams.

Alcohol Extract.—This was a dark resinous mass, and amounted to only 4 grams. No crystalline substance could be obtained from it.

Isolation of Convolvulinolic Acid, $C_{14}H_{28}(OH).CO_2H$.
(*Hydroxypentadecylic Acid.*)

The above-mentioned petroleum extract, which was strongly acid to litmus, was mixed with water, and carefully neutralized with sodium hydroxide. The solution was then concentrated on a water bath, and, after filtering, was allowed to stand for some time, when a crystalline sodium salt separated. This was collected, dried on a porous plate, then dissolved in water, and the solution acidified with hydrochloric acid, when the organic acid separated in a solid state. It was collected on a filter, dried, and then crystallized three times from a mixture of light petroleum and ether, the solution being cooled in a freezing mixture of ice and salt. The acid then separated in the form of small, fine needles, which melted at 51–52°.

0.1288 gave 0.3284 CO_2 and 0.1416 H_2O. C = 69.5; H = 12.2.
$C_{15}H_{30}O_3$ requires C = 69.7; H = 11.6 per cent.

A portion of the acid was converted into a silver salt, and the latter analyzed.

0.1970 of salt gave on ignition 0.0580 Ag. Ag = 29.4.
$C_{15}H_{29}O_3$ Ag requires Ag = 29.6 per cent.

It is thus evident that the above-described acid possesses the formula $C_{15}H_{30}O_3$, and that it is identical with an acid of the same composition previously described by Taverne[1] as a hydroxypentadecylic acid (m. p. 50.5°) and by Hoehnel[2] as convolvulinolic acid (m. p. 51.5°). The latter designation appears, however, to have been given first by Mayer[3] and subsequently by Kromer,[4] to products obtained from jalap resin by methods analogous to that above described, but to which different formulas were assigned, and which were obviously not pure substances.

Methyl Convolvulinolate, $C_{14}H_{28}(OH).CO_2CH_3$.—One gram of convolvulinolic acid was dissolved in methyl alcohol, and the solution saturated with dry hydrogen chloride. After allowing the liquid to stand over night, it was poured into water, and the mixture extracted with ether, the ethereal liquid being washed with a dilute solution of sodium carbonate, then with water, dried, and the solvent removed. A light yellow, viscid product was thus obtained, which was distilled under diminished pressure, when it passed over as a colorless oil. On allowing the latter to stand, it solidified to a mass of small needles, which, after drying on a porous plate, melted at 32–33°.

---

[1] *Rec. trav. chim. Pays Bas,* **13,** 187 (1894); *J. Chem. Soc. Abst.,* **68,** i, 119 (1895).

[2] *Arch. Pharm.,* **234,** 674 (1896).

[3] *Ann.,* **83,** 121 (1852).

[4] *J. Chem. Soc. Abst.,* **66,** i, 540 (1894).

0.0940 gave 0.2420 CO_2 and 0.1012 H_2O. C = 70.2; H = 11.9.
$C_{16}H_{32}O_3$ requires C = 70.6; H = 11.8 per cent.

This substance was thus quite pure methyl convolvulinolate. It appears to have first been prepared by Taverne,[1] who has recorded its boiling point as 206–208°/15 mm., and its melting point as 35°.

Isolation of Ipurolic Acid, $C_{13}H_{25}(OH)_2.CO_2H$.

The above-mentioned ether extract, obtained from the product of the action of dilute sulphuric acid on the alcohol extract of the hydrolyzed resin, was a soft, dark brown mass. It was mixed with water, and carefully neutralized with sodium hydroxide. The solution was then concentrated on a water-bath, and allowed to cool, when a sodium salt separated in a partially crystalline condition. This salt was twice recrystallized from water, after which it was decomposed by hydrochloric acid, and the resulting acid extracted by means of ether. The solid thus obtained was twice recrystallized at a low temperature from a mixture of ether and chloroform, after which it melted at 94–95°. On subsequently crystallizing twice from the same mixture of solvents, and finally from chloroform, the melting point was raised to 100–101°.

0.1120 gave 0.2648 CO_2 and 0.1094 H_2O. C = 64.5; H = 10.8.
$C_{14}H_{28}O_4$ requires C = 64.6; H = 10.8 per cent.

A silver salt of the acid was also prepared and analyzed.

0.1496 of salt gave on ignition 0.0436 Ag. Ag = 29.1.
$C_{14}H_{27}O_4$ Ag requires Ag = 29.4 per cent.

The above-described substance was thus identified as ipurolic acid, $C_{13}H_{25}(OH)_2.CO_2H$, which was first isolated by the authors from the stems of *Ipomoea purpurea*, Roth.[2] When mixed with the acid obtained from the latter source, the melting point remained unchanged.

Methyl Ipurolate, $C_{13}H_{25}(OH)_2.CO_2CH_3$.—This was prepared by the method previously described.[3] When crystallized from dilute methyl alcohol it separated in fine, colorless needles, melting at 68–69°.

0.1070 gave 0.2562 CO_2 and 0.1056 H_2O. C = 65.3; H = 10.9.
$C_{15}H_{30}O_4$ requires C = 65.7; H = 10.9 per cent.

It may be noted in this connection that Hoehnel[4] has designated that portion of the product of the alkaline hydrolysis of "convolvulin" which is insoluble in ether as "convolvulic acid," and has assigned to it the formula $C_{45}H_{80}O_{28}$. He has furthermore assumed that the formation of convolvulinolic acid, $C_{15}H_{30}O_3$, from the last-mentioned product by its acid hydrolysis may be expressed by the following equation:

---

[1] *Loc. cit.*

[2] *Am. J. Pharm.*, 80, 273 (1908).

[3] *Loc. cit.*, p. 275.

[4] *Arch. Pharm.*, 234, 684 (1896).

$$C_{45}H_{80}O_{28} + 5H_2O = 5C_6H_{12}O_6 + C_{15}H_{30}O_3.$$

It has been shown, however, by this investigation that the portion of the product of the alkaline hydrolysis of the resin which was not only insoluble in ether, but which had also been deprived of constituents soluble in chloroform and ethyl acetate, when submitted to the action of dilute sulphuric acid, yielded, besides sugar and convolvulinolic acid, a number of other acids, among which formic, butyric, valeric, and ipurolic acids were identified. A portion of the product, moreover, is apparently not glucosidic, and remains after the treatment with sulphuric acid in the form of an organic acid which is readily soluble in water. It is obvious, therefore, that the formation of all these substances can not be expressed by a simple equation, and that the amorphous product designated as "convolvulic acid" can by no means be regarded as an individual substance, which is capable of being represented by a chemical formula.

Oxidation of the Alcohol Extract of the Hydrolyzed Resin with Nitric Acid.

Ten grams of the previously described alcohol extract of the hydrolyzed resin were dissolved in a little water, and about 100 grams of nitric acid (sp. gr. 1.4) added. A vigorous reaction soon ensued, and when this had subsided the mixture was heated for a time, after which water was added, and the heating continued for about 10 minutes. On allowing the liquid to cool, a quantity of substance was deposited, which was extracted with ether, and the ethereal liquid then shaken with a solution of sodium carbonate. The ether was subsequently dried and evaporated, when only a slight oily residue was obtained. The sodium carbonate liquid was acidified and extracted with ether, the ethereal liquid being dried and the solvent removed, when 1.4 grams of an oily product were obtained, which soon solidified to a perfectly white, crystalline mass. This was repeatedly crystallized from water, when two principal fractions were obtained, melting at 105–106° and 122–125° respectively. The final mother liquor contained a small amount of an acid which was freely soluble in water, and was evidently oxalic acid.

The fraction melting at 105–106° consisted of long, flat needles, and was analyzed with the following result:

0.1072 gave 0.2266 CO_2 and 0.0844 H_2O. C = 57.6; H = 8.7.
$C_9H_{16}O_4$ requires C = 57.4; H = 8.5 per cent.

This substance was thus identified as azelaic acid, the melting point of which has been recorded as 106°.

The fraction melting at 122–125° was obtained in the form of small needles, and gave on analysis the following result:

0.0768 gave 0.1676 CO_2 and 0.0658 H_2O. C = 59.5; H = 9.5.
$C_{10}H_{18}O_4$ requires C = 59.4; H = 8.9 per cent.

This substance was evidently sebacic acid, the melting point of which has been variously stated as 127–128° and 133–133.5°.

By the oxidation of convolvulinolic acid with potassium permanganate, as also with nitric acid, Hoehnel[1] obtained, besides a valeric acid, a crystalline, dicarboxylic acid of the composition $C_{10}H_{18}O_4$ (m. p. 109°), which he has designated as ipomic acid ("ipomsäure"), and regards it as isomeric with sebacic acid. The name of *ipomic* or *ipomoeic* acid was first given by Mayer[2] to a product obtained by the action of nitric acid on that portion of jalap resin which is insoluble in ether, and which he designated "convolvulin." The acid obtained by Mayer was stated to agree with the formula $C_5H_9O_2$, and to melt at 104°. Neison and Bayne,[3] who repeated the experiment of Mayer, have shown, however, that the so-called ipomoeic acid is identical with sebacic acid, for by the oxidation of material designated by them as "jalapin" they obtained an acid melting at 126–127°, and agreeing in all respects with sebacic acid, the melting point of which they record as 127–128°. This fact appears not to have been considered by Hoehnel,[4] who has retained the name of "ipomsäure" for a substance which was evidently somewhat impure sebacic acid. The present investigation has shown, moreover, that the sebacic acid obtained as above described is accompanied by a lower homologue, namely, azelaic acid. A mixture of these two acids was likewise obtained, as already noted, from the product of the fusion of the alcohol extract of the resin with potassium hydroxide.

Summary.

In view of the extended experimental details of this investigation, a summary of the more important results may here be given.

The material employed consisted of an original bale of jalap tubers of good quality. On completely extracting the jalap with hot alcohol, and subjecting the resulting extract to distillation with steam, a small amount of an *essential oil* was obtained. This oil was at first of a pale yellow color, but became very dark on standing. The odor was smoky and disagreeable. It distilled between 80 and 160°/60 mm., had a density of 0.8868 at 20°/20°, and was optically inactive.

The portion of the extract which was soluble in water contained chiefly coloring matter and sugar, the latter yielding *d*-phenylglucosazone

---

[1] *Arch. Pharm.*, 234, 679 (1896).

[2] *Ann. Chem. Pharm.*, 83, 143 (1852); 95, 160 (1855).

[3] *J. Chem. Soc.*, 27, 729 (1874).

[4] *Loc. cit.*

(m. p. 217–218°). The portion of the extract insoluble in water represents the product known as "resin of jalap," which is recognized by most of the national Pharmacopoeias. The amount of this resin contained in the drug, as indicated by a special assay of the latter, corresponded to 9.4 per cent. of its weight, and 11.6 per cent. of it was soluble in ether. The total crude resin, when purified by means of animal charcoal, had a specific optical rotation of —37.0°. On extracting the crude resin successively with (I) light petroleum (b. p. 40–60°), (II) ether, (III) chloroform, (IV) ethyl acetate, and (V) alcohol, a number of products were obtained, the examination of which has shown the resin to be of much more complex composition than has previously been assumed.

I. *Petroleum Extract of the Resin.*—This represented 1.9 per cent. of the total resin. It contained palmitic and stearic acids in a free state, and, after hydrolysis, yielded formic, butyric and higher volatile acids, palmitic acid, and a mixture of unsaturated acids, which appeared to consist chiefly of linolic acid. From the unsaponifiable portion of the extract there were obtained a phytosterol, $C_{27}H_{46}O$ (m. p. 134–135°; $[\alpha]_D$ —32.4°), cetyl alcohol, $C_{16}H_{34}O$, and a small amount of a substance melting at 56–57°, which agrees in composition with the formula $C_{18}H_{38}O$. This *substance*, which appears to be a new compound, yields color reactions similar to those of the phytosterols.

II. *Ether Extract of the Resin.*—This represented 9.7 per cent. of the total resin. From it there was isolated a small amount of a new, dihydric alcohol, which possesses the formula $C_{21}H_{32}O_2(OH)_2$, and is designated *ipurganol*. Ipurganol crystallizes in colorless needles, melting at 222–225°, and has, in pyridine solution, $[\alpha]_D$ —44.9°. It yields color reactions similar to those given by the phytosterols. *Diacetylipurganol*, $C_{21}H_{32}O_4(CH_3.CO)_2$, forms colorless leaflets, melting at 166–167°, and has, in pyridine solution, $[\alpha]_D$ —36.0°. The ether extract, after treatment with alkalis and dilute sulphuric acid, yielded, furthermore, a little phytosterol and cetyl alcohol, small amounts of volatile acids, and a quantity of amorphous products.

III. *Chloroform Extract of the Resin.*—This represented 24.1 per cent. of the total resin. From it there was isolated a very small amount of β-methylaesculetin, $C_9H_5(CH_3)O_4$. After treatment with alkalis and dilute sulphuric acid this extract yielded, furthermore, formic, butyric, and *d*-methylethylacetic acids, together with convolvulinolic acid, $C_{15}H_{30}O_3$, and apparently a higher homologue of the latter. Glucose was also produced by this treatment, thus indicating that a portion of the extract was of a glucosidic nature.

IV. *Ethyl Acetate Extract of the Resin.*—This represented 22 per cent. of the total resin. On treatment with dilute alcoholic sulphuric acid, it yielded formic, butyric, and *d*-methylethylacetic acids, together with convolvulinolic acid, $C_{15}H_{30}O_3$, and apparently a higher homologue of the latter, having the composition $C_{17}H_{34}O_3$. It also yielded, besides indefinite amorphous products, a considerable quantity of a sugar, which was evidence that at least a portion of the extract was of a glucosidic nature.

V. *Alcohol Extract of the Resin.*—This represented 38.8 per cent. of the total resin. After treatment with animal charcoal it was obtained in the form of a nearly white powder, which melted at 150–160°, and had $[\alpha]_D$ —37.1°. When fused with potassium hydroxide it yielded formic, acetic, butyric, valeric, and higher volatile acids, together with azelaic and sebacic acids. When subjected to alkaline hydrolysis with baryta it yielded, besides small amounts of formic and butyric acids, *d*-methylethylacetic acid, $C_5H_{10}O_2$ (b. p. 174–176°; $[\alpha]_D$ +17.55°), together with a quantity of an amorphous product, readily soluble in water, which may be designated as the hydrolyzed resin. This has now been shown to be of very complex composition, for by successive extraction with (*a*) ether, (*b*) chloroform, (*c*) ethyl acetate, and (*d*) alcohol it is capable of being resolved into a number of products.

(*a*) *Ether Extract of the Hydrolyzed Resin.*—This extract, on heating with dilute sulphuric acid, yielded formic, butyric, and other acids, together with sugar.

(*b*) *Chloroform Extract of the Hydrolyzed Resin.*—This extract, like the preceding one, yielded small amounts of formic, butyric, and other acids, together with sugar.

(*c*) *Ethyl Acetate Extract of the Hydrolyzed Resin.*—This extract, on heating with dilute sulphuric acid, yielded formic, butyric, *d*-methylethylacetic, and other acids, together with sugar.

(*d*) *Alcohol Extract of the Hydrolyzed Resin.*—This extract could be obtained in the form of a nearly colorless powder, which melted at 110–115°, and had $[\alpha]_D$ —33.53°. When heated with dilute sulphuric acid it yielded, in addition to sugar, small amounts of formic, butyric, and valeric acids, together with convolvulinolic and ipurolic acids. The last-mentioned acid possesses the formula $C_{13}H_{25}(OH)_2.CO_2H$, and was first obtained by the authors from the stems of *Ipomoea purpurea*, Roth.[1] By the oxidation of this extract with nitric acid, azelaic and sebacic acids were obtained.

Each of the above-described extracts of the hydrolyzed resin appeared to be only partly glucosidic, and to contain a readily soluble organic acid which was unaffected by the treatment with dilute sulphuric acid.

Physiological Tests.

The extracts obtained by the treatment of the original jalap resin with various solvents, as above described, were kindly tested for us with respect to their physiological action by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, and our thanks are due to him for the assistance rendered in this connection.

---

[1] *Am. J. Pharm.*, 80, 273 (1908).

One gram of each of the extracts was administered to dogs, with the following results:

1. The petroleum extract had no effect.
2. The ether extract produced prompt, but not severe purgation.
3. The chloroform extract caused repeated purgation, lasting for 48 hours.
4. The ethyl acetate extract was similar in its action to the chloroform extract, the purgation lasting 24 hours.
5. The alcohol extract produced repeated and powerful purgation.

Apart from the purgative action of the various extracts no effect was observed, all the animals having remained perfectly well. It was furthermore concluded by Dr. Dale that the apparent differences in the degree of action of the extracts II, III, IV, and V cannot be regarded as of great importance in view of individual differences with respect to the action of drugs, and of purgatives in particular.

The product resulting from the alkaline hydrolysis of the alcohol extract of the resin, consisting of acids readily soluble in water, had no effect when administered to a dog in doses of 1 gram. This result is in accordance with the observations previously recorded respecting an analogous but less completely purified product from jalap resin, which has been designated "convolvulic acid."[1]

Conclusions.

In considering the results of this investigation, some of the more important facts and deductions may specially be noted.

In the first place, it has been shown that the resin of jalap is of much more complex composition than has hitherto been assumed, and that none of the amorphous products obtained from it possess the attributes of a homogeneous substance. It follows that the formulas which have heretofore been assigned to products such as the so-called convolvulin, purgic acid, convolvulic acid, etc., are devoid of any significance or scientific value, and they should therefore no longer be retained in chemical literature. The same considerations will doubtless apply to the various amorphous products obtained from other convolvulaceous resins to which distinctive names and formulas have been assigned.

In the present investigation of jalap resin, as already indicated, a number of substances have been obtained which permitted of definite identification or characterization. It is evident, however, that the formation of these substances, when resulting from the degradation of an amorphous product of the resin, can by no means be expressed by simple chemical equations.

---

[1] Compare Husemann, "Die Pflanzenstoffe," 2nd edit., 1882, p. 1141.

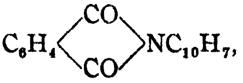
It may finally be observed that the purgative action of jalap resin is not due to any single or well-defined constituent, inasmuch as the products obtained by its successive extraction with various solvents, with the exception of the portion removed by light petroleum, appear to possess about an equal degree of physiological activity.

ACTION OF AMINES ON PHTHALIC ACID. VI.[1]

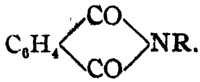
By J. Bishop Tingle and B F. Parlett Brenton.

Received November 2, 1909.

In the course of the work described in our earlier paper, we studied the interaction of phthalic anhydride on a number of amino derivatives other than those we have already mentioned. The products which we ultimately obtained did not prove to be suitable for our intramolecular rearrangement investigations and consequently we did not carry on the work with them very far. We desire, however, to record the results which we have obtained, because we cannot continue our experiments conjointly.

Camphylamine and phthalic anhydride, when melted together, gave what is probably the *imide*,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NC_{10}H_7$, m. 54°. No solid hydrolysis product (amidic acid) could be obtained from it.

Benzidine and phthalic anhydride, under similar conditions, yielded a highly insoluble compound of great stability.

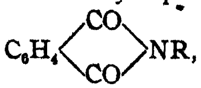
We made a large number of experiments with the object of "fixing" the mobile amidic hydrogen atom in the amidic acids, $RNHCOC_6H_4CO_2H$. With phosphorus pentachloride, phosphorus trichloride, or thionyl chloride, the only stable product of the reaction was the imide  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NR$. We then directed our attention to the preparation of acylated amidic acids, such as $CH_3CONRCOC_6H_4CO_2H$. We attempted to prepare them by the action of acyl chlorides and of acid anhydrides on the amidic acids and also from acyl amines and phthalic anhydride. We found, however, that acetyl chloride or acetic anhydride either failed to react with the amidic acids, or else it transformed them into the imide, behaving in this respect exactly like the phosphorus halides mentioned above. Most of our experiments were made with phthalphenylamidic acid. Our attempts at synthesis were carried out with phthalic anhydride and acetanilide, *p*-acetotoluidide and formo-β-naphthalide, respectively. When fractionally recrystallized, the products gave fairly sharp melting points, but further investigation showed that we were dealing with mixtures and that the phthalic anhydride, so far as it reacts at all, simply displaces the acetyl or formyl group from the amine, phthal-β-naphthylimide, for example, being produced from the above formo-β-naphthalide.

---

[1] The previous papers bearing on this subject have appeared as follows: Bishop Tingle and Cram, *Am. Chem. J.*, 37, 596 (1907); Bishop Tingle and Lovelace, *Ibid.*, 38, 642 (1907); Bishop Tingle and Rolker, This Journal, 30, 1882 (1908); Bishop Tingle and Brenton, *Ibid.*, 31, 1157 (1909); Bishop Tingle and Bates, 31, 1233 (1909).

We failed to obtain any crystalline compound from 2,4-diaminophenol and phthalic anhydride, but from *m*-aminobenzoic acid we prepared the dicarboxylic acid, $HO_2\overset{1}{C}C_6H_4\overset{3}{N}HCO\overset{1}{C}_6H_4\overset{2}{C}O_2H$.[1]

The interaction of carbamide and of certain of its alkyl derivatives with phthalic anhydride has been studied previously.[2] When the mixture of the two compounds is heated in a test tube it melts, becomes solid as the temperature is raised and finally liquefies again. During the heating gas is evolved almost continuously, but chiefly towards the later stages of the experiment. The gas consists of ammonia and carbon dioxide, or in the case of a thiocarbamide, of carbon oxysulphide. The solid product of the reaction is a phthalimide,



$C_6H_4\langle{}^{CO}_{CO}\rangle NR$, in a fairly pure condition. After being once recrystallized it shows the correct melting point. This method of preparing the compounds in question is so easy and requires so little time that it is obviously the best to employ for the preparation, in relatively small quantity, of the imides in which $R = H$, CH_3, C_2H_5, or some other group, the amino or halide derivative of which is very volatile. We experimented with carbamide and its methyl, ethyl, benzyl and phenyl derivatives, and also with phenylthiocarbamide, obtaining phthalimide, and phthalmethyl-, ethyl-, benzyl- and phenylimides, respectively. Ethylidene carbamide gave only a tar. In the course of our experiments with phenylcarbamide we were successful in isolating phthalphenylamidic acid, $C_6H_5NHCO C_6H_4CO_2H$, as an intermediate product. Its formation throws some light on the mechanism of the reaction. To accomplish this was one of the chief objects of our investigation.

We have made some experiments, of a preliminary nature, on the action of aniline and 4,5-dichlorophthalic acid. The results show that the substances react in a more complicated manner than in the case of aniline and phthalic acid.

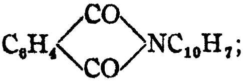
Experimental.

1. *Camphylamine and Phthalic Anhydride.*—When these substances

---

[1] Gabriel. Puitti, *Ber.*, 16, 1320.

[2] Piutti, *Ann.*, 214, 20. Dunlap, *Am. Chem. J.*, 18, 337.

are fused together, in molecular proportion, water is evolved. The product appears to be *phthalcamphylimide*,  $C_6H_4\langle{CO \atop CO}\rangle NC_{10}H_7$; after being recrystallized from benzene it melts at 54°.

N found, 5.67; calculated, 4.94 per cent.

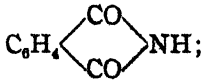
The substance was warmed with an aqueous solution of sodium carbonate and the clear solution acidified; this caused the deposition of an oil.

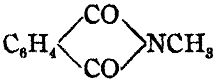
2. *Benzidine and Phthalic Anhydride.*—When melted together these substances combine. The resulting compound is very sparingly soluble in all the ordinary media. It was dissolved in nitrobenzene and precipitated by benzene, but we are uncertain as to its purity because it remained unmelted at 300°. Our specimen contained 7.37 per cent. of nitrogen. It failed to react with benzoyl chloride, by the Schotten-Baumann method. In a similar experiment, employing 2 mols. of base : 1 mol. of anhydride, the product appeared to be similar to that obtained in the first experiment, or identical with it.

3. *Acetanilide, p-Acetotoluidide, Formo-β-Naphthalide and Phthalic Anhydride.*—As explained in the theoretical part of this paper, our experiments with these substances were carried out in the hope of preparing disubstituted phthalamidic acids, $RR'NCOC_6H_4CO_2H$, in which one of the groups, R or R', could be easily removed. The acylated bases were melted with the anhydride, and the heating continued during varying periods ranging from a few minutes to 1.5 hours. The resulting materials, after recrystallization, usually melted within 1°, but, in each case, further purification caused the melting point to vary widely from that shown at first and the analytical results were not constant. From formo-β-naphthalide we were able to isolate and identify phthal-β-naphthylimide and to prove that formic acid was evolved during the heating. It is evident, therefore, that the phthalyl group merely replaces the acyl already linked to the nitrogen of the amine.

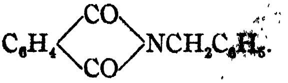
4. *2,4-Diaminophenol and Phthalic Anhydride.*—A considerable number of experiments were carried out with these substances, but no definite compound could be isolated.

5. *m-Aminobenzoic Acid and Phthalic Anhydride.*—We prepared the dicarboxylic acid, $HO_2\overset{1}{C}C_6H_4\overset{3}{N}H\overset{1}{C}OC_6H_4\overset{2}{C}O_2H$, in the manner described above and purified it by means of its sodium salt from the strongly colored materials which are produced during its formation. It dissolved readily in ethyl alcohol (40 per cent.), but the deposited material failed to exhibit crystalline structure. It was recovered unchanged by boiling with acetic anhydride and also by treatment with benzoyl chloride, by the Schotten-Baumann method.

6. *Carbamide and Phthalic Anhydride.*—When these substances are mixed in equimolecular proportion and heated they melt, then after a time solidify and, finally, as the temperature is raised, become liquid again. During the heating ammonia and carbon dioxide are evolved vigorously. The product consists of phthalimide,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH$; it was fully identified by its melting point and analytical results. The same substance was obtained by the use of 2 molecular proportions of carbamide, under otherwise similar conditions. The yield was almost quantitative.

7. *Methylcarbamide and Phthalic Anhydride.*—These substances, when treated in the same manner as the carbamide, behaved similarly, giving phthalmethylimide,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NCH_3$ (m. p. 132°), carbon dioxide and ammonia. The yield was almost quantitative.

8. *Ethylcarbamide and Phthalic Anhydride.*—The product in this case was phthalethylimide. The yield was relatively small.

9. *Benzylcarbamide and Phthalic Anhydride.*—These substances reacted like the methylcarbamide, the product being phthalbenzylimide,  $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NCH_2C_6H_5$. The yield was good. An unsuccessful attempt was made to isolate the intermediate compound, the formation of which is indicated by the molten mass becoming solid. The only materials which could be identified were the mother-substances.

10. *Phenylcarbamide and Phthalic Anhydride.*—When these substances are melted together and the heating stopped as soon as they solidify, the product consists of phthalphenylamidic acid, $C_6H_5NHCOC_6H_4CO_2H$, which was fully identified. In another experiment the heating was continued until all reaction had ceased. In this case the only substance which was obtained was phthalphenylimide.

11. *Phenylthiocarbamide and Phthalic Anhydride.*—These substances behaved exactly like the phenylcarbamide mixture, except that the gases which were evolved were ammonia and carbon oxysulphide.

12. *Ethylidenecarbamide and Phthalic Anhydride.*—The product from this experiment was tarry.

The results recorded above show that the preparation of phthalimide and its alkyl derivatives is carried out far more easily by means of the carbamides than by the use of the amines, or from the alkyl halides and potassium phthalimide, provided that only relatively small quantities of material are required (5–10 grams) and that the amine or alkyl derivative is so volatile as to require the use of a sealed tube or autoclave.

13. *Aniline and 4,5-Dichlorophthalic Acid.*—A number of preliminary experiments have been made with these compounds. The results show that the conditions require much more careful regulation than in the case of phthalic acid.

Summary.

1. We have studied the action of phthalic anhydride on a number of amines, including camphylamine, which gives the camphylimide; benzidine, which forms an insoluble product; and *m*-aminobenzoic acid, which yields a dicarboxylic acid.
2. The acylated amines, acetanilide, *p*-acetotoluidide and formo-β-naphthalide, eliminate the acyl group when heated with phthalic anhydride.
3. Carbamide and certain alkyl- and arylcarbamides, including phenylthiocarbamide, eliminate ammonia and carbon dioxide (or carbon oxysulphide) and form phthalimides or phthalamidic acids.

It is intended to continue the investigation of the interaction of phthalic acids and amines in this laboratory during the coming year.

McMaster University, Toronto, Canada.

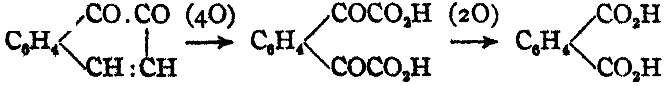
NOTE ON THE OXIDATION OF β-NAPHTHOQUINONE.

By C. H. Robinson.

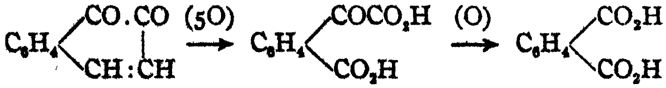
Received November 1, 1909

In a series of experiments on the oxidation of naphthalene and various naphthalene derivatives, Daly[1] found some indications that in the oxidation of β-naphthoquinone by potassium permanganate in alkaline solution the reaction ceased before the amount of permanganate had been reduced which would correspond to the oxidation of the naphthoquinone to phthalonic acid and he mentions the possibility of the diketo acid, $C_6H_4(COCO_2H)_2$, being formed in the solution. Under the direction of Professor Allan, the author investigated this reaction in the hope of preparing the diketo acid in this way.

If the oxidation in alkaline solution were to the diketo acid and then in acid solution to phthalic acid the two stages of the reaction might be represented by A, but if the oxidation in alkaline solution were to phthalonic acid they would be represented by B.

A.


$$C_6H_4\left\langle\begin{matrix}CO.CO\\ |\quad\ |\\ CH:CH\end{matrix}\right. \xrightarrow{(4O)} C_6H_4\left\langle\begin{matrix}COCO_2H\\ \\ COCO_2H\end{matrix}\right. \xrightarrow{(2O)} C_6H_4\left\langle\begin{matrix}CO_2H\\ \\ CO_2H\end{matrix}\right.$$

B.


$$C_6H_4\left\langle\begin{matrix}CO.CO\\ |\quad\ |\\ CH:CH\end{matrix}\right. \xrightarrow{(5O)} C_6H_4\left\langle\begin{matrix}COCO_2H\\ \\ CO_2H\end{matrix}\right. \xrightarrow{(O)} C_6H_4\left\langle\begin{matrix}CO_2H\\ \\ CO_2H\end{matrix}\right.$$

---

[1] *J. Phys. Chem.*, 11, 105.

So that the ratio of the amounts of oxygen used in the two stages of the reaction would be two according to A or five according to B.

The β-naphthoquinone was prepared by the method of Lagodzinski and Hardine[1] and purified by the method given by Boswell.[2] It is slightly soluble in decinormal sodium bicarbonate solution (0.54 g. per liter) and not more soluble in a normal solution.

To find the ratio between the amount of permanganate required to oxidize the naphthoquinone in alkaline solution and the permanganate required to complete the oxidation in acid solution to phthalic acid, 110 cc. of a saturated solution of the quinone in decinormal sodium bicarbonate was added to 50 cc. decinormal permanganate solution and left at laboratory temperature for twenty-four hours. In 50 cc. of this solution the residual permanganate was determined by adding a solution of 0.4 g. potassium iodide and 2 g. sulphuric acid in 100 cc. water and titrating the iodine set free. To another 50 cc. of the solution two per cent. sulphuric acid and a few drops of manganese sulphate solution were added, and after two minutes, by which time the oxidation to phthalic acid was complete, the solution of potassium iodide and sulphuric acid was added and the iodine determined. Since the oxidizing power of the permanganate is 1.66 times greater in acid solution than in alkaline solution, the permanganate used in oxidizing the solution to phthalic acid was multiplied by 1.66 so that the amounts of permanganate would be in proportion to their oxidizing value.

	I.	II.
$\frac{\text{Permanganate reduced in alkaline solution}}{\text{Permanganate reduced in acid solution}}$	4.65	4.75

This shows conclusively that the oxidation is as represented above in B and that the reaction in alkaline solution proceeds to phthalonic acid, but it is still possible that there is a rapid oxidation to the diketo acid and then a slower oxidation to phthalonic acid.

Some experiments were made to determine the constituents of the solution at various stages of the oxidation by adding small amounts of permanganate to the quinone solution, allowing the reaction to proceed till all the permanganate was reduced, acidifying the solution and ethering out. As the residual quinone is so much more insoluble in water than the products of the reaction, the residue obtained by the evaporation of the ether contained little else than quinone.

A = initial weight of quinone in the solution.
B = cc. permanganate used to 50 cc. quinone solution.
C = weight of residue from ether.
D = weight of quinone which would be left if oxidation were direct to phthalonic acid.

---

[1] *Ber.*, 27, 3075.

[2] This Journal, 29, 230.

E = weight of quinone which would be left if oxidation were to diketo acid.

A. Gram.	B. cc.	C. Gram.	D. Gram.	E. Gram.
0.0226	1	0.0209	0.0210	0.0206
0.0226	6	0.0126	0.0131	0.0108
0.0226	8	0.0110	0.0100	0.0068
0.0226	10	0.0087	0.0069	0.0023

The results given in this table are not very good because the method was inaccurate but they confirm the conclusion arrived at from the previous experiments that there is no intermediate stage in the oxidation of β-naphthoquinone to phthalonic acid in alkaline solution. A series of experiments, in which the rate of oxidation of the quinone in alkaline solution was determined, also gave no indication of the existence of an intermediate product.

Further experiments to prepare the diketo acid by the saponification of phthalyl cyanide are now being carried out.

UNIVERSITY OF TORONTO.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 174.]

RESEARCHES ON QUINAZOLINES (TWENTY-FOURTH PAPER). ON OXALYL ANTHRANILIC COMPOUNDS AND QUINAZOLINES DERIVED THEREFROM.[1]

BY MARSTON TAYLOR BOGERT AND ROSS AIKEN GORTNER.

Received November 27, 1909.

In 1883, Kretschy[2] obtained by oxidation of kynurine, or of kynurenic acid, an acid which he called "kynuric acid." The succeeding year[3] he showed that this "kynuric acid" was oxalyl anthranilic acid.

The following pages describe various derivatives of oxalyl anthranilic acid and condensation products obtained therefrom.

Mauthner and Suida[4] have recorded the fact that when anthranilic acid is heated with ethyl oxalate, both oxalyl dianthranilic acid and ethoxalyl anthranilic acid are produced:

$$\mathrm{HOOC.C_6H_4.NH_2 + ROOC.COOR = HOOC.C_6H_4.NHCOCOOR + ROH,}$$

$$\mathrm{2HOOC.C_6H_4.NH_2 + ROOC.COOR =}$$
$$\mathrm{HOOC.C_6H_4.NHCOCONH.C_6H_4.COOH + 2ROH,}$$

and we have used this method for the preparation of these substances, as well as for the methoxalyl anthranilic acid. Oxalyl dianthranilic acid was also prepared by the action of oxalyl chloride upon anthranilic acid.

---

[1] Read at the meeting of the New York Section, March 5, 1909.

[2] *Monatsh. Chem.*, 4, 157 (1883).

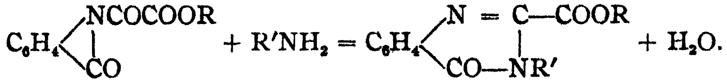
[3] *Ibid.*, 5, 30 (1884).

[4] *Monatsh. Chem.*, 9, 743 (1888).

By the action of acetic anhydride, these acyl anthranils were changed to acyl anthranils,

$$\overline{\text{OC.C}_6\text{H}_4\text{.N}}\text{COCOOR and } \overline{\text{OC.C}_6\text{H}_4\text{.N}}\text{COCO}\overline{\text{N.C}_6\text{H}_4\text{.CO}},$$

which were then treated with various primary amines to get the corresponding quinazolines:[1]



$$\text{C}_6\text{H}_4\left<\begin{matrix}\text{NCOCOOR}\\ |\\ \text{CO}\end{matrix}\right. + \text{R'NH}_2 = \text{C}_6\text{H}_4\left<\begin{matrix}\text{N} = \text{C—COOR}\\ \quad\quad |\\ \text{CO—NR'}\end{matrix}\right. + \text{H}_2\text{O}.$$

The reactions with the methoxalyl and ethoxalyl anthranils resulted in the formation of the expected quinazolines, the amines used being ammonia, methylamine, aniline, β-naphthylamine, hydrazine and phenylhydrazine.

Some of the results are, however, rather puzzling. Thus, when ethoxalyl anthranil was heated with alcoholic ammonia, the product was the ammonium salt of the quinazoline acid, $\overline{\text{HN.CO.C}_6\text{H}_4\text{.N} = \text{C}}\text{.COONH}_4$; but when the anthranil was fused with urea, or boiled with an alcoholic solution of urea, the quinazoline ester was obtained, $\overline{\text{HN.CO.C}_6\text{H}_4\text{.N} = \text{C}}$.COOR.

Ethoxalyl anthranil, heated with an alcoholic solution of methylamine, gave the quinazoline amide, $\text{CH}_3\overline{\text{N.CO.C}_6\text{H}_4\text{N} = \text{C}}\text{.CONHCH}_3$, and hydrazine similarly gave a hydrazide. Aniline, β-naphthylamine, and phenylhydrazine, on the other hand, did not displace the ester group, but gave quinazoline esters, even when the reaction was pushed to the point where a second molecule of the amine condensed with the keto group of the quinazoline to an anil, $\text{C}_6\text{H}_5\text{N.C(:NC}_6\text{H}_5\text{).C}_6\text{H}_4\text{.N} = \text{C.COOR}$.

Experimental.

Methoxalyl Anthranilic Acid, $(1)\text{HOOC.C}_6\text{H}_4\text{.NHCOCOOCH}_3(2)$.—An equimolecular mixture of anthranilic acid and methyl oxalate was heated at 140–55°. The mixture melted, methyl alcohol distilled off, and after 30 minutes' heating a hard cake remained. This was pulverized fine, washed with cold water and the residue repeatedly extracted with dilute alcohol. From the alcoholic extracts, combined and concentrated, crystals were obtained which on recrystallization from water melted at 176.5° (corr.). For analysis, they were further purified by recrystallization from a mixture of alcohol and benzene, washed with ligroin, and dried at 110°.

---

[1] Anschütz, Schmidt and Greiffenberg, *Ber.*, 35, 3480 (1902). Bogert and Chambers, THIS JOURNAL, 27, 649 (1905). Bogert and Seil, *Ibid.*, 27, 1305 (1905). Bogert and Steiner, *Ibid.*, 27, 1327 (1905), *et al.*

Calculated for $C_{10}H_9O_5N$: N, 6.27.
Found: N, 6.17.

The acid dissolves readily in cold sodium carbonate solution with evolution of carbon dioxide. It is also soluble in hot water, alcohol, or benzene; difficultly soluble in cold water, practically insoluble in chloroform or ligroin.

In this preparation, some oxalyl dianthranilic acid is also formed.

Ethoxalyl Anthranilic Acid, (1)$HOOC.C_6H_4.NHCOCOOC_2H_5$(2).—Mauthner and Suida[1] have already reported on the formation of this compound from anthranilic acid and ethyl oxalate. It was, however, first obtained by von Baeyer[2] by oxidizing ethyl indoxylate with sulphuric acid and potassium dichromate. von Baeyer gives its melting-point as 180–1°.

Twenty grams anthranilic acid were mixed with slightly more than an equimolecular amount of ethyl oxalate and the mixture heated for an hour at 140–50°, followed by ten minutes further heating at 160°. When cold, the melt was pulverized and extracted with boiling water. From the hot aqueous extract, colorless needles of ethoxalyl anthranilic acid separated on cooling, melting sharply at 184° (corr.). Yield, 27 grams. From the residue insoluble in water, 1.4 grams oxalyl dianthranilic acid were isolated.

Oxalyl Dianthranilic Acid (*Oxanilide Di-o-carbonic Acid*), (1)$HOOC.C_6H_4.NHCOCONH.C_6H_4.COOH$(2).—That this acid is formed by heating together anthranilic acid and ethyl oxalate has already been noted by Mauthner and Suida.[1]

We prepared it by heating 1 molecule of methyl or ethyl oxalate with 2 molecules of anthranilic acid for half an hour to an hour at 140–155°, removing methoxalyl- or ethoxalyl anthranilic acid by extracting the crude product with boiling water and dilute alcohol. We also prepared it by dissolving anthranilic acid in dry benzene and adding oxalyl chloride. The reaction was violent, with evolution of copious fumes of hydrochloric acid, and the precipitate was purified by washing (digestion) with benzene and with alcohol.

The purified products obtained by the above methods were identical. The substance is a white powder, decomposing at about 330° (uncorr.), and is insoluble in the ordinary neutral organic solvents. When freshly prepared from methyl oxalate, it seems to be appreciably soluble in alcohol, but on standing becomes practically insoluble in it.

Methoxalyl Anthranil, $\overline{OC.C_6H_4.N}.COCOOCH_3$.—Methoxalyl anthranilic acid was boiled for several minutes with excess of acetic anhydride and the solution then concentrated to crystals. These crystals were pressed dry on a porous plate and recrystallized from dry benzene. They then melted sharply at 177.5° (corr.). As the methoxalyl anthranilic acid has a melting point very close to this (176.5° corr.), it was thought at first that we had only recovered the original substance unaltered, but on mixing with some of the methoxalyl anthranilic acid, the melting point was lowered to 150° (uncorr.). The pure dry substance gave the following figures on analysis:

---

[1] *Loc. cit.*

[2] *Ber.*, 15, 777 (1882).

Calculated for $C_{10}H_7O_4N$: N, 6.83.
Found: N, 7.02.

This anthranil crystallizes from dry benzene or acetic anhydride in pale brownish needles. It is very sensitive to moisture, being hydrolyzed to methoxalyl anthranilic acid by ordinary commercial absolute alcohol (99.8 per cent.) or by ordinary glacial acetic acid.

Ethoxalyl Anthranil, (1)$OC.C_6H_4.N.COCOOC_2H_5$, was prepared in similar manner from the ethoxalyl anthranilic acid and acetic anhydride. Recrystallized from acetic anhydride, it forms large, colorless plates, melting at 129–130° (corr.). Yield, 81 per cent. of the theoretical.

Calculated for $C_{11}H_9O_4N$: N, 6.40.
Found: N, 6.67.

In contrast with the above methyl derivative, this ethoxalyl anthranil is not very easily hydrolyzed. It may even be recrystallized from relatively dilute alcohol without suffering any extensive hydrolysis. Boiling water rapidly hydrolyzes it to the ethoxalyl anthranilic acid again.

Oxalyl Dianthranil, $OC.C_6H_4.N.COCON.C_6H_4.CO$. — Five grams oxalyl anthranilic acid were boiled for three hours with excess of acetic anhydride, the solid changing from white to yellow. The insoluble material was filtered out and washed with acetic anhydride. Yield, 3.4 grams. For analysis, this crude product was boiled again for three hours with acetic anhydride, washed with the anhydride, and dried at 110°.

Calculated for $C_{16}H_8O_4N_2$: C, 65.75; H, 2.74; N, 9.59.
Found: C, 65.20, 64.97, 65.81; H, 3.20, 2.87, 3.05; N, 9.98.

The purified oxalyl dianthranil is a yellow powder, melting with decomposition at about 345° (uncorr.), and is insoluble in the ordinary neutral solvents. Boiling water slowly hydrolyzes it to anthranilic and oxalic acids. It is readily hydrolyzed by hot concentrated hydrochloric acid.

4-Quinazolone-2-carboxylic Acid (4-Hydroxyquinazoline-2-carboxylic Acid), $HN.CO.C_6H_4.N = C.COOH \rightleftarrows N = C(OH).C_6H_4.N = C.COOH$.

Ammonium Salt, $C_8H_5ON_2.COONH_4$.—Two grams ethoxalyl anthranil were added to a slight excess of ammonia dissolved in 95 per cent. alcohol. The anthranil dissolved with evolution of heat and a white precipitate suddenly separated. The mixture was heated to 100°, the precipitate filtered out and washed repeatedly with 95 per cent. alcohol. Yield of this ammonium salt, nearly theoretical.

Calculated for $C_9H_9O_3N_3$: N, 20.28.
Found: N, 20.26.

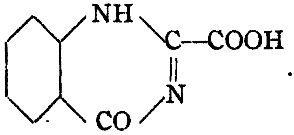
The ammonium salt crystallizes from water in long silky colorless needles, melting at 229° (corr.) with evolution of ammonia and carbon dioxide.

Free Acid.—Cold concentrated hydrochloric acid was added to the ammonium salt and then water. The free acid separated in a gelatinous condition and was crystallized from dilute alcohol. White silky needles resulted, softening at 227° and melting with evolution of carbon dioxide at 230° (corr.). The melt on cooling congealed in colorless needles, and re-melted at 214° (corr.). The melting point of 4-quinazolone (4-hydroxyquinazoline) as found by different investigators is variously stated from 209 to 216.5°.

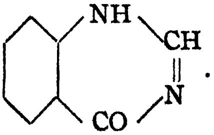
Calculated for $C_9H_6O_3N_2$: N, 14 73.
Found: N, 14.97.

The acid is easily soluble in hot alcohol, only slightly soluble in benzene, and very difficultly soluble in water. Boiled with mineral acids, it gradually loses carbon dioxide.

In 1885, Griess[1] described a compound which he called "carboxylcyanamidobenzoyl," and to which he assigned the formula



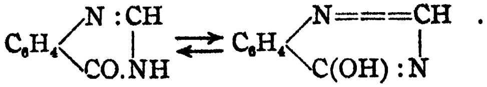
When this acid was heated, Griess found that it lost carbon dioxide giving another substance, which he named "carbimidamidobenzoyl" and formulated thus



Subsequent investigations of Weddige,[2] Knape,[3] Bischler and Burkart,[4]

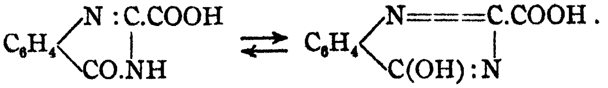
[1] *Ber.*, 18, 2418 (1885).
[2] *J. prakt. Chem.*, [2] 31, 124 (1885).
[3] *Ibid.*, 43, 227 (1891).
[4] *Ber.*, 26, 1349 (1893).

Niementovski,[1] and Bogert and Hand[2] showed that this "carbimidamidobenzoyl" was the simple 4-quinazolone and should be formulated



$$C_6H_4\left\langle\begin{matrix}N:CH\\ |\\ CO.NH\end{matrix}\right. \rightleftarrows C_6H_4\left\langle\begin{matrix}N{=\!=\!=}CH\\ |\\ C(OH):N\end{matrix}\right. .$$

From this it follows that the formula for "carboxylcyanamidobenzoyl" should be written



$$C_6H_4\left\langle\begin{matrix}N:C.COOH\\ |\\ CO.NH\end{matrix}\right. \rightleftarrows C_6H_4\left\langle\begin{matrix}N{=\!=\!=}C.COOH\\ |\\ C(OH):N\end{matrix}\right. .$$

Reissert and Grube[3] have recently obtained this same acid by the rearrangement in dilute acid solution of *o*-cyanoxanilic acid, $NC.C_6H_4.NHCOCOOH$.

Griess describes his acid as crystallizing in leaflets, but gives no melting point. Reissert and Grube, like ourselves, obtained the acid in needles. They give a melting point of 201–202°. We do not understand how they found so low a melting point, unless they did not recrystallize their product sufficiently. It does not appear from the article that they recrystallized their compound to constant melting point.

Ethyl Ester, $C_8H_5ON_2.COOC_2H_5$.—1.5 grams ethoxalyl anthranil and 0.42 gram urea were melted together at 125°. The temperature was then raised slowly to 140–150° and kept there for an hour. The cold melt was extracted with alcohol, and from the alcoholic extracts on cooling a crystalline material separated which was filtered out, washed with water and dried. The same substance was obtained when ethoxalyl anthranil (1 gram) and urea (0.33 gram) were boiled together in alcohol solution. For analysis, the compound was recrystallized from alcohol and dried at 110°.

Calculated for $C_{1}H_{10}O_3N_2$: N, 12.83.
Found: N, 12.90.

It crystallizes from alcohol in minute colorless needles, melting at 185.5° (corr.), and is insoluble in water or in mineral acids. It dissolves easily in solutions of the caustic alkalies, but not in strong sodium carbonate solution. Heated with aqueous ammonia, the ammonium salt of the acid (described above) results, apparently without any amide. That alcohol is split off by the action of alkalies was shown by the iodoform test.

3-Methyl-4-quinazolone-2-carbomethylamide, $CH_3N.CO.C_6H_4.N = C.CONHCH_3$.—One molecule of ethoxalyl anthranil was added to an aqueous solution of slightly more than 2 molecules methylamine, and the solution concentrated to small bulk. On standing several days, beautiful pale-rose prisms separated, melting sharply at 160° (corr.). They were dried at 110° and analyzed:

---

[1] *J. prakt. Chem.*, [2] 51, 564 (1895).

[2] This Journal, 24, 1048 (1902).

[3] *Ber.*, 42, 3713 and 3715 (1909).

Calculated for $C_{11}H_{11}O_2N_3$: N, 19.35.
Found: N, 19.51.

The compound is very soluble in water; much less soluble in alcohol.

Methyl 3-Phenyl-4-quinazolone-2-carboxylate, $C_6H_5N.CO.C_6H_4.N = C.COOCH_3$.—0.5 gram methoxalyl anthranil was mixed with a slight excess of aniline and the mixture heated carefully with the naked flame. As soon as the boiling commenced, the flame was removed and the action allowed to continue without further heating. Water was evolved and, on cooling, the mixture solidified. It was extracted with dilute alcohol, and from this extract small colorless plates separated on cooling, m. p. 203.5° (corr.) with previous softening in the neighborhood of about 120° (uncorr.). The yield was very poor. For analysis, the compound was recrystallized from dilute alcohol and dried at 110°.

Calculated for $C_{16}H_{12}O_3N_2$: N, 10.0.
Found: N, 9.78.

The ester is easily soluble in alcohol, but very slightly soluble in water. Heated with excess of aniline, it gives a difficultly soluble compound, probably similar to the anil described beyond.

Ethyl 3-Phenyl-4-quinazolone-2-carboxylate, $C_{14}H_9ON_2.COOC_2H_5$.—0.5 gram ethoxalyl anthranil was heated for a few minutes with excess of aniline, and the mass then cooled and extracted with 95 per cent. alcohol. Colorless plates separated from the alcoholic extract on cooling.

Calculated for $C_{17}H_{14}O_3N_2$: N, 9.50.
Found: N, 9.40.

This ester melts at 160° (corr.). It is but slightly soluble in water, easily soluble in alcohol. In cold potassium hydroxide solution, it is apparently insoluble, but dissolves on warming. It is not hydrolyzed readily by hot concentrated hydrochloric acid.

Ethyl 3-Phenyl-4-phenyliminoquinazoline-2-carboxylate,

$C_6H_5N.C(:NC_6H_5).C_6H_4.N = C.COOC_2H_5$.—This anil is obtained simultaneously with the above ester from the interaction of ethoxalyl anthranil and excess of aniline. If the heating is continued many minutes, the yield of anil is good. It can be separated easily from the keto ester by its insolubility in alcohol. For analysis, it was washed repeatedly with hot alcohol and dried at 110°.

Calculated for $C_{23}H_{19}O_2N_3$: N, 11.36.
Found: N, 11.40.

It is a colorless crystalline powder, insoluble in water and in all the ordinary neutral organic solvents. It melts with effervescence at 291° (corr.).

Ethyl 3-β-Naphthyl-4-β-naphthyliminoquinazoline-2-carboxylate,

$C_{10}H_7N.C(: NC_{10}H_7).C_6H_4.N = C.COOC_2H_5$.—0.5 gram ethoxalyl anthranil and 0.5 gram β-naphthylamine were carefully melted together, and the temperature then gradually raised to the boiling point. The melt was allowed to cool, and was then thoroughly extracted with 95 per cent. alcohol. The insoluble residue was dried at 110° and analyzed.

Calculated for $C_{31}H_{23}O_2N_3$: N, 8.95.
Found: N, 8.83.

It is a grayish crystalline powder, insoluble in water, ethyl or amyl alcohol, acetone or benzene, and melts to an amber liquid at 253–4° (corr.).

Ethyl 3-Anilino-4-quinazolone-2-carboxylate, $C_6H_5NHN.CO.C_6H_4.N = C.COOC_2H_5$.—An equimolecular mixture of ethoxalyl anthranilic acid and phenylhydrazine was heated to boiling. Water was evolved, but there was no evidence of any alcohol being given off. On cooling, a clear amber glass resulted. This was crystallized from alcohol, and the crystals obtained washed with dilute alcohol. Recrystallized from alcohol, long lemon-yellow needles were obtained, melting at 142° (corr.).

Calculated for $C_{17}H_{15}O_3N_3$: N, 13.58.
Found: N, 13.65.

The compound is insoluble in water, but dissolves readily in alcohol, benzene or acetone, giving bright yellow solutions. It is insoluble in cold solutions of caustic alkalies, but dissolves on heating. It does not dissolve in dilute mineral acids.

Sym. Di-(3-amino-4-quinazolone-2-carboxylic Acid) Hydrazide,

$H_2NN.CO.C_6H_4.N = C.CONHNHCO.C = N.C_6H_4.CO.NNH_2$.—One gram of hydrazine hydrate (in 50 per cent. aqueous solution) was diluted with 95 per cent. alcohol, 2 grams ethoxalyl anthranil gradually stirred in, and the mixture heated to boiling. The undissolved substance turned light yellow. It was filtered out and the yellow filtrate on standing deposited an additional amount of this same yellow amorphous material. It is slightly soluble in the ordinary neutral organic solvents, and melts at 157–158° (corr.) with loss of ammonia, thereby becoming insoluble and infusible. Yield, 2.1 grams. For analysis, it was recrystallized from a large volume of absolute alcohol, and dried at 110°.

Calculated for $C_{18}H_{14}O_4N_6$: N, 27.60.
Found: N, 27.91.

Treated with acetic anhydride, a thick sirup resulted which defied all attempts to crystallize or purify it.

The same hydrazide was produced when methoxalyl anthranil was used instead of the ethoxalyl compound. Varying the proportions of anthranil and hydrazine did not appear to affect the result.

2-Carbazino-3-amino-4-quinazolone, $H_2N\overline{N.CO.C_6H_4.N = C}.CONHNH_2$, was obtained from its hydrochloride (see below) by dissolving the latter in water, adding potassium hydroxide solution to alkalinity and then acidifying with acetic acid. The precipitated free base was washed with water and crystallized from dilute alcohol acidified with acetic acid. Beautiful transparent plates were obtained, carrying water of crystallization. This water of crystallization was driven out at 100–110°, and the crystals then became opaque and melted at 202.5° (corr.).

Calculated for $C_9H_8O_2N_5$: N, 31.96.
Found: N, 31.70.

The substance is appreciably soluble in water and easily soluble in alcohol. When once dissolved, it does not separate again readily, and the loss on recrystallization is therefore considerable. A small amount tends to precipitate in an amorphous state.

Hydrochloride, $C_9H_8O_2N_5.3HCl$.—One gram ethoxalyl anthranil was added to an aqueous solution of half a gram hydrazine hydrate diluted with 95 per cent. alcohol, and the mixture heated to boiling. The above *sym.* diquinazolone hydrazide (m. 157–158°) separated. Without removing the latter, concentrated hydrochloric acid was poured in and the mixture again boiled. The colorless hydrochloride which separated was washed with 95 per cent. alcohol. Yield, 0.8 gram. For analysis, it was recrystallized from a mixture of dilute hydrochloric acid and alcohol, washed with alcohol, and dried at 110°.

Calculated for $C_9H_8O_2N_5.3HCl$: N, 21.43.
Found: N, 21.97.

It is freely soluble in water, but insoluble in most of the ordinary organic solvents, and melts at 190–191° (corr.). From strong hydrochloric acid, it crystallizes in colorless needles. As this monohydrazide is presumably formed by the hydrolysis of the dihydrazide which first separated, there should be produced simultaneously the 3-amino-4-quinazolone-2-carboxylic acid, but we have been unable to isolate any such compound from the mother liquors.

Acetyl Derivative, $CH_3CONH\overline{N.CO.C_6H_4.N = C}.CONHNHCOCH_3$.—0.8 gram 2-carbazino-3-amino-4-quinazolone hydrochloride and 0.6 gram fused sodium acetate were added to an excess of acetic anhydride and the solution boiled down to small bulk. More acetic anhydride was then added, the precipitated salt (NaCl) filtered out, and the filtrate boiled down twice more with acetic anhydride, finally carrying the evaporation to dryness. The residual clear amber glass was dissolved in 95 per cent. alcohol, the solution concentrated and benzene added. The acetyl derivative separated in a fine yellowish powder, and was washed thoroughly with benzene and dried. Yield, 0.35 gram.

Calculated for $C_{13}H_{13}O_4N_5$: N, 23.10.
Found: N, 23.16.

The pure substance melts at 125° (corr.). It is easily soluble in water, alcohol or chloroform, but does not crystallize well from these solvents, evaporation of the solvent leaving finally a clear glass. On long boiling with benzene, small transparent plates were obtained, carrying benzene of crystallization.

Attempts to eliminate water from this compound and condense the side chains to a cycle proved unsuccessful.

NEW YORK, N. Y.

PREPARATION OF CHOLINE AND SOME OF ITS SALTS.

By R. R. RENSHAW.

Received November 22, 1909.

In connection with some work on the bactericidal properties of lecithins the author had occasion to prepare some of the salts of choline. In looking through the literature it was found that the choline used in recent investigations was prepared and isolated by methods which it was thought might be simplified.

Wurtz in 1867[1] prepared choline by heating trimethylamine with an excess of ethylene chlorohydrin, and later (1868) he and also Griess and Harrow[2] (1885) obtained it by the action of a concentrated solution of trimethylamine on ethylene oxide. The products were purified by means of the gold salt.

Later investigators have used different procedures or new methods. In 1889 Bode[3] made choline by the prolonged action of dilute nitric acid on bromomethyltrimethylamine bromide which he had made from ethylene bromide by Hofmann's method. No yield was given. Gulewitsch in 1898[4] in an extended article on choline described its preparation in quantity by a modification of Wurtz's method. Redistilled anhydrous ethylene chlorohydrin in large excess was heated with a 15–20 per cent. solution of trimethylamine in absolute alcohol for 24 hours in a water bath. The choline from the resulting slightly acid solution was separated partly as the mercuric, and partly as the platinic chloride double salts. Yield, 61 per cent. Krüger and Bergell in 1903[5] got choline by the action of water on bromocholine bromide at 160° for 4 hours. No yield given. A large number of investigators have prepared choline from egg lecithin. For the most part these later methods are either tedious or give poor yields or both.

---

[1] *Compt. rend.*, 65, 1015; *Ann. Spl.*, 6, 116.

[2] *Ber.*, 18, 707 (1885).

[3] *Ann.*, 267, 268.

[4] *Z. physiol. Chem.*, 24, 509.

[5] *Ber.*, 36, 2901.

The author has found that a practically quantitative yield (97.3 per cent.) of choline chloride can be obtained by the following method. Fourteen grams of freshly distilled anhydrous ethylene chlorohydrin were placed in a bomb tube cooled to —12 to —20° (saturated salt solution and snow). Trimethylamine, generated by dropping a concentrated solution of its hydrochloride (18 grams) on solid sodium hydroxide, was passed through a U-tube containing solid potassium hydroxide and then through a freezing bath into the ethylene chlorohydrin contained in the bomb tube. If the amine hydrochloride was added slowly, practically complete condensation ensued. After all the hydrochloride had been added the generating flask was warmed gently and air passed through slowly. The tube was then sealed and heated two hours at 80–90° when the contents had completely crystallized. On opening the tube after a further two hours' heating there was a little pressure due to a slight excess of trimethylamine. The contents, composed of perfectly white, well-formed crystals, were washed a number of times with dry ether, and allowed to stand for some time in a vacuum desiccator. The product so obtained, while sufficiently pure for most purposes, still contained too high a percentage of chlorine—probably due to a slight amount of ethylene chlorohydrin held mechanically in or on the crystals. A pure product was obtained by dissolving in absolute alcohol and adding ether gradually until complete precipitation was obtained. The fine white needle crystals were filtered, washed with ether, and dried in a vacuum.

Choline Acetate was prepared by neutralizing an aqueous solution of the base (obtained by the action of moist silver oxide on choline chloride) with acetic acid. Very long evaporation under high vacuum at 50° and cooling caused the product to crystallize to a fan-shaped mass of needle crystals. These were extremely hydroscopic, and practically insoluble in carbon disulphide, benzene, petroleum ether, acetone and ethyl ether; very soluble in alcohol and water. Choline acetate is very easily hydrolyzed.

Choline Sulphate, $(HOCH_2CH_2N(CH_3)_3)_2(SO_4)$, prepared by the action of silver sulphate on choline chloride, separates from a very concentrated aqueous solution in short needles. The salt was purified by evaporating to dryness under high vacuum at 50–100° (almost no decomposition occurred), dissolving in alcohol, filtering, adding petroleum ether and refrigerating. Perfectly white well-formed needle crystals separated out. These were practically insoluble in carbon disulphide, ether, benzene and petroleum ether; easily soluble in alcohol and water. The sulphate is fairly hydroscopic.

Calculated for $(HOCH_2CH_2N(CH_3)_3)_2SO_4$: S, 10.52 per cent.
Found: S, 10.63, 10.77 per cent.

Choline Dihydrogen Phosphate, $HOCH_2CH_2N(CH_3)_3H_2PO_4$.—On agitating a concentrated solution of choline chloride with silver phosphate and filtering from the excess of silver phosphate and silver chloride, a very basic solution was obtained, indicating that the tricholine phosphate was largely hydrolyzed. A dilute solution of phosphoric acid was added to permanent acidity. The ratio of phosphate ions to the choline was then practically 1 : 1. The solution was evaporated under high vacuum at 80–90° to a horny mass. The product was purified by extracting with boiling absolute alcohol in which the phosphate is slightly soluble. By this means beautiful, long white, fairly hydroscopic needle crystals were obtained, which were practicably insoluble in benzene, carbon disulphide, petroleum ether, acetone and ethyl ether; slightly soluble in alcohol; very soluble in water. After washing in ether and drying in a vacuum desiccator the product was analyzed.

Calculated for $HOCH_2CH_2N(CH_3)_3H_2PO_4$: P, 15.42 per cent.
Found: P, 15.48 per cent.

The chemistry of the choline derivatives is being further investigated by the author.

WESLEYAN UNIVERSITY, MIDDLETOWN, CONN

BACTERICIDAL PROPERTIES OF LECITHINS AND CHOLINE SALTS.

BY R. R. RENSHAW AND K. N. ATKINS.

Received November 22, 1909.

There is some disagreement in the literature concerning the bactericidal properties of lecithins. The existence of cobra lecithides, the speculation regarding a possible relation between lecithin and the amboceptors,[1] and, among others, the fact that such a product as fresh milk, containing certain amounts of lecithins, has some germicidal constituent, gives interest to the problem in question. In view of this the authors have attempted to determine what influence, if any, lecithins might have upon the growth of some of the more common organisms. Along with this, since it is possible that the presence of a decomposition product, *i. e.*, choline, might have been responsible for the disagreement, a few of its salts were prepared and their bactericidal properties determined.

The procedure was as follows: Pure cultures of the different organisms were grown at room temperature for about twelve hours in an ordinary broth medium. One loopful of this was transferred to a flask containing about 50 cc. of the same kind of medium. After a thorough shaking this second broth culture was divided among small bottles holding 9 cc. of the medium. In the experiments on milk the raw fresh product was used. To the different bottles of the culture or milk 1 cc. of a 4 per cent. emulsion of lecithin or 4 per cent. solutions of the different choline salts were added. One bottle was used as a control. After the organisms had developed 12 hours, 1 cc. of the medium was withdrawn from each bottle by means of a sterile pipette and transferred to sterile water blanks of either 9 or 99 cc., making a dilution of 10 or 100. The water blanks were then thoroughly shaken and if higher dilutions were to be used, as was true in most cases, 1 cc. of the diluted culture was transferred to a second water blank and again thoroughly shaken. In this way the proper dilution was reached. Anticipating from other experiments the approximate number of bacteria which would develop under given conditions the dilution was so calculated as to allow accurate counting of the plates. Knowing that the number of bacteria in milk kept for 24 hours at 19° would be large (in fact the product was almost sour) the dilution here used was as high as 1,000.000. In all cases 1 cc. of this finally diluted culture was plated out in agar, incubated for 24–48 hours at 37° and counted. The agar medium used contained 1.2 per cent. agar-agar and its acidity was equivalent to 1 per cent. normal acid.

---

[1] Kyes, *Z. physiol. Chem.*, 41, 273.

Commercially pure samples of lecithins were repurified by several precipitations from alcoholic solutions by means of acetone and subsequent drying in a vacuum desiccator. The concentration of the emulsions was low, about 0.4 per cent. This, however, is greater than is usually found in biological fluids.

With some of the organisms, especially typhoid, a large number of series were made. The following tables are composed of representative determinations. The figures in each are the average counts of ten to a dozen plates.

In several series the organisms were plated out after incubating 6 or 24 hours. It was found, however, that a twelve-hour period was the best.

B. LACTIS AEROGENES.

	12°.		19°.	
	0 hrs. x 1000.	12 hrs. x 1000.	0 hrs. x 1000.	12 hrs. x 1000.
Control	5.0	8.0	2.5	140.0
Lecithin	5.0	7.0	2.5	135.0
Choline chloride	5.0	8.7	2.5	128.0
Choline phosphate	5.0	5.4	2.5	132.0
STAPH. PYOGENES ALBUS.				
Control	1.4	7.0	1.3	15.0
Lecithin	1.4	6.0	1.3	12.0
Choline chloride	1.4	6.0	1.3	14.0
Choline phosphate	1.4	5.0	1.3	17.0

MILK.

	12°.		19°.	
	0 hrs. x 1000.	12 hrs. x 1000.	0 hrs. x 1000.	12 hrs. x 1000,
Control	15.0	160.0	120.0	112,000.0
Lecithin	15.0	160.0	120.0	95,000.0
Lecithin (2)	15.0	100.0	.....	....
Choline chloride	15 0	140.0	120.0	104,000.0
Choline phosphate	....	.....	120.0	108,000.0
COLI.				
Control	6.0	9.0	20.0	4,000.0
Lecithin	6.0	7.0	20.0	2,400 0
Choline chloride	6.0	10.0	20.0	3,500.0
Choline phosphate	6.0	9.0	20.0	3,200.0
TYPHOID.	(15°).			
Control	23.0	290.0	4.8	137.0
Lecithin	23.0	260.0	4.8	113.6
Choline chloride	23.0	270.0	4.8	105.0
Choline phosphate	23.0	270.0	4.8	127.0

As indicated in the tables, there is, in general, a varying retardation in the development of bacteria in the cultures containing lecithins, although this is not marked in some cases. In fact, in looking over the records of individual plates, it was found that in about 10 per cent. of over two hundred plates no change at all was shown, or there was a very slight increase in the development. Nevertheless, we are inclined to attribute slight bactericidal properties to lecithins at these dilutions, although for practical purposes this is negligible.

In general an effect by choline salts was less frequently observed and with them the diminution was less marked.

WESLEYAN UNIVERSITY, MIDDLETOWN, CONN.
DEPARTMENT OF CHEMISTRY.

[FROM THE DIVISION OF CHEMISTRY, HYGIENIC LABORATORY, U. S. PUBLIC HEALTH AND MARINE HOSPITAL SERVICE, WASHINGTON, D. C.].

FURTHER STUDIES ON THE APPLICATION OF THE VOLHARD METHOD TO THE ESTIMATION OF ALKALOIDS.

BY ELIAS ELVOVE.

Received November 15, 1909.

It has been pointed out by the writer[1] that the difficulty experienced by many workers in obtaining suitable indicators in the alkalimetric estimation of alkaloids and the necessity for using a comparatively large number of such indicators, each more or less suitable to one or only a few alkaloids, may be completely overcome if we adopt the very simple modification of the usual procedure and substitute hydrochloric acid as the solvent for the alkaloid instead of sulphuric acid which is usually employed.[1] That is, instead of dissolving the isolated free alkaloid in a measured excess of sulphuric acid and determining the excess of acid with the aid of the indicator best suitable for that particular alkaloid, the latter is dissolved in an excess of hydrochloric acid and the excess of acid got rid of by simple evaporation on the water bath, thus obtaining a salt of the alkaloid which, as long pointed out by Plugge[2] and others, may in many cases be estimated with the aid of phenolphthalein as indicator and hence indirectly also the amount of alkaloid. Further, that by thus converting the alkaloids into their hydrochlorides it becomes possible to estimate the alkaloids indirectly through a determination of the chlorine by the beautiful and exact Volhard method. In this way, in addition to avoiding the necessity for using a comparatively large number of different indicators, each more or less suitable to one or only a few alkaloids, we are supplied with a means for estimating such alkaloids as do not react very sharply with any of the indicators thus far studied. Thus of the eleven different indicators which Kippenbeger studied,[3] namely, lacmoid, iodeosine, uranin, cochineal, azolitmin, haematoxylin, methyl orange, ethyl orange, phenolphthalein, alkannin, and Congo red, the only ones which he found to lend themselves in any way for use in the titration of quinine were azolitmin and haematoxylin. The applicability, however, of azolitmin to quinine titrations is denied by Rammstedt;[4] while the misleading results obtainable when haematoxylin is used as indicator in titrating cinchona alkaloids may be seen from the results obtained by Hille,[5] who states that under circumstances which should require 1.3 cc. of 0.1 *N* acid, one may be in doubt as to the end reaction to the extent of making an error equivalent to a whole cubic centimeter of the 0.1 *N* solution, which would make the error about 77 per cent. It is probably owing to this apparent lack of a suitable indicator in titrating cinchona alkaloids that the U. S. Pharmacopoeia (1905), at present official, recommends a gravimetric process in all assays[1] where these alkaloids are involved, although it is a recognized fact[2] that the alkaloidal residues obtained in the course of assay frequently contain considerable neutral non-alkaloidal matter, and hence, probably on this account, titration with standard acid is recommended in the cases of most of the other pharmacopoeial alkaloidal assays. Finally, it was pointed out[3] that such procedure applied to the alkaloids would also conclusively show the exact relative acidity of the various alkaloids and the apparent uncertainty[4] as to the exact relative acid-combining power of such alkaloids as quinine and strychnine, for example, would be entirely cleared up.

---

[1] Bull. 54, Hyg. Lab., U. S. Pub. Health and Mar. Hosp. Serv., Wash.

---

[1] See U. S. Pharmacopoeia (1905), pp. 28, 67, 107, 143, 146–7, 197, 200, 300, 340, 344. Kippenberger, *Z. anal. Chem.*, 39, 201–229 (1900). Kebler, THIS JOURNAL, 17, 822–831 (1895).

[2] *Arch. Pharm.*, [3] 25, 45–59 (1887).

[3] *Loc. cit.*

[4] *Apoth. Zeit.*, 22, 1117 (1907).

[5] *Arch. Pharm.*, 241, 106 (1903). Hille expresses himself in this connection as follows: "Da angenommen wird, das 50 g. genau $^2/_3$ der Chloroform-Aether-Flüssigkeit ist, sollen zur Bindung der Alkaloide 1,3 cm. Säure verbraucht sein. Der Endpunkt der Titration ist nun aber bei Anwendung von Haematoxylin als Indicator sehr schwierig zu erkennen. Ich habe viele Dutzend Titrationen mit Haematoxylin als Indicator auszuführen versucht. Es ist niemals mit Sicherheit zu sagen: Jetzt ist der Farbenumschlag eingetreten. Man wird im allgemeinen bei Anwendung von 1/10 Normallösungen innerhalb eines ganzen Kubikzentimeters im Zweifel sein, ob der Farbenumschlag eingetreten ist oder nicht. Nimmt man jedoch den Punkt als richtig an, wo eben die Flüssigkeit anfängt, die Farbe etwas zu verändern, so bekommt man viel zu niedrige Resultate, wie ich mit reinen Alkaloiden nachgewiesen habe. Von dieser ersten Farbenänderung an ändert sich mit jedem Tropfen 1/10 Normal-Kalilauge die Färbung etwas, so dass man immer im Zweifel ist, wann der richtige Punkt eingetreten ist. Titrationen welche ich mit reinen Alkaloiden ausführte, ergaben Resultate von 85–115 per cent. der angewandten Menge."

Recently, Poirrier blue has been recommended by Beckurts and Runne[5] as a better indicator than phenolphthalein in the titration of the salts of such alkaloids as cocaine and also that in certain cases phenolphthalein may be used to better advantage as an indicator if the titration be carried out on an alcoholic solution of the alkaloidal salt instead of the aqueous solution, so that the means for estimating the salts of the alkaloids are still further increased and hence also the advantages of converting the alkaloid into a salt for the purpose of indirectly estimating the alkaloid. However, all these advantages, important as they may be, are nevertheless much more limited in practical application than appears to be the case with the application of the Volhard method for this same purpose. For as pointed out by Plugge[3] and as may be seen from the tabulated results given in the subsequent part of this paper, phenolphthalein does not in all cases afford the means for close quantitative estimation, so that in such cases the results thus obtained are of approximate value only and serve chiefly in indicating about how much standard silver nitrate it will be necessary to add in the subsequent estimation by the Volhard method. On the other hand, the procedure involving the Volhard method affords also the additional advantage of permitting the estimation to be carried out even where it is impossible or difficult to obtain a colorless solution of the alkaloidal residue or its salt—an occurrence which is quite frequently met with in alkaloidal assaying—since by converting the estimation of the alkaloid into a simple determination of the chlorine in sodium chloride which is what the procedure here described practically amounts to, we are no longer dependent on the alkaloidal properties of the alkaloid and hence where its presence interferes it usually may be got rid of by adding sufficient alkali to unite with all of the hydrochloric acid in the solution and filtering off the precipitated alkaloid; or the alkaloid, as well as other organic coloring matter may be got rid of by gentle ignition of the residue obtained on evaporating the solution containing the metallic chloride or the measured excess of standard silver solution. In the previous work[1] along this line, it was shown that this procedure is applicable to the alkaloids quinine, quinidine, cinchonine, cinchonidine, and strychnine. Now the results obtained with eight more alkaloids which are frequently met with commercially, namely, the alkaloids cocaine, morphine, codeine, narcotine, atropine, hydrastine, pilocarpine, and brucine, are presented.

---

[1] U. S. Pharmacopoeia (1905), pp. 156, 174, 462.

[2] See Kebler, THIS JOURNAL, 17, 830–831 (1895).

[3] *Loc. cit.*

[4] See Schimpf, "Manual of Volumetric Analysis," 5th ed., pp. 502 and 498. Also tables of equivalents in U. S. Pharmacopoeia (1905), pp. 555, 567, 568.

[5] *Apoth. Ztg.* (*Berlin*), 24, 662–663 (1909).

General Mode of Procedure.

Solutions of the respective alkaloids in hydrochloric acid of approximately half-normal strength were carefully prepared so as to make the solution of fiftieth molar strength (one-fiftieth of the molecular weight in grams per liter) with respect to the alkaloid. Varying amounts (5 to 50 cc.) of these solutions were transferred into porcelain evaporating dishes and the latter with their contents placed on the water bath, where they were allowed to remain until the liquid had completely evaporated. To each residue there were then added 5 cc. of alcohol (99 per cent.), with which it was thoroughly stirred and mixed, and the liquid again allowed to completely evaporate on the water bath, when this treatment with 5 cc. of alcohol was repeated. In the case of the alkaloids previously studied, the remaining excess of hydrochloric acid was gotten rid of by simply allowing the residue to remain on the water bath three hours after the liquid had completely evaporated. This latter mode of getting rid of the remaining excess of hydrochloric acid while requiring a longer time than the alcohol treatment is nevertheless simpler in some respects since it requires practically no attention The chief reason, however, for adopting here the alcohol treatment is because it was found that in the case of some of the alkaloids (*e. g.*, cocaine) considerable of the combined hydrochloric acid is lost if the former procedure is applied. After the second evaporation with the alcohol, the residue was taken up with distilled water (usually 10 cc.), phenolphthalein added, and the acidity of the solution titrated with 0.1 *N* sodium hydroxide. Wherever precipitation occurred on addition of the alkali, the precipitated alkaloid was filtered off, washed with small amounts of water until on testing a drop of the filtrate with silver nitrate it was shown to be free from chlorine, and the chlorine in the solution determined by the Volhard method. The latter was carried out as follows: The solution was diluted to about

---

[1] *Loc. cit.*

70 cc. with distilled water, then acidified by adding 5 cc. of dilute (10 per cent.) nitric acid, and followed by a measured amount of standard silver nitrate solution which was a little (2 cc.) in excess of that theoretically required. The whole was then made up to a definite volume (100 cc.), filtered through a dry filter, and an aliquot portion (50 cc.) of the filtrate taken for the determination of the excess of silver remaining in solution. The filtering off of the precipitate which usually forms on adding the standard alkali is in most cases unnecessary but was here carried out with all the alkaloids in order to make the procedure more nearly uniform in all cases. With the comparatively larger amounts of brucine the color developed in the solution on addition of the nitric acid interferes in the subsequent determination of the excess silver. Hence in those cases an aliquot portion was evaporated to dryness on the water bath, the residue ignited, then taken up with hot dilute nitric acid and the excess of silver in the solution determined by means of standard thiocyanate in the usual way. The results obtained are given in the following tables.

Cocaine.—A 0.02 *M* solution of cocaine in dilute hydrochloric acid of approximately half-normal strength was prepared, containing 1.212 grams cocaine, $C_{17}H_{21}NO_4$, in 200 cc. The results obtained with this solution are given in Table I.

TABLE I.—EFFECT OF VARYING THE AMOUNT OF COCAINE ON THE CONSTANCY OF THE PROPORTION OF HCl IN THE ALKALOIDAL RESIDUE.

0.02 *M* cocaine taken. cc.	0.1 *N* NaOH required. cc.	0.1 *N* $AgNO_3$ required. cc.	Amount of HCl found.[1] Milligrams.	Theory for $C_{17}H_{21}NO_4.HCl$. Milligrams.
5	0.85	0.96	3.40	3.54
10	2.00	2.00	7.09	7.09
20	4.20	4.10	14.53	14.18
30	6.25	5.96	21.13	21.27
40	8.45	7.90	28.00	28.36
50	11.60	10.24	36.30	35.45

Morphine.—A 0.02 *M* solution of morphine in dilute hydrochloric acid of approximately half-normal strength was prepared, containing 1.140 grams morphine, $C_{17}H_{19}NO_3$, in 200 cc. The results obtained with this solution are given in Table II.

TABLE II.—EFFECT OF VARYING THE AMOUNT OF MORPHINE ON THE CONSTANCY OF THE PROPORTION OF HCl IN THE ALKALOIDAL RESIDUE.

0.02 *M* morphine taken. cc.	0.1 *N* NaOH required. cc.	0.1 *N* $AgNO_3$ required. cc.	Amount of HCl found. Milligrams.	Theory for $C_{17}H_{19}NO_3.HCl$. Milligrams.
5	0.70	1.00	3.54	3.54
10	1.40	2.00	7.09	7.09
20	3.82	4.02	14.25	14.18
30	5.80	5.96	21.13	21.27
40	7.80	8.00	28.36	28.36
50	9.80	10.00	35.45	35.45

[1] All calculations were based on the amount of $N/10$ $AgNO_3$ required.

Codeine.—A 0.02 *M* solution of codeine in dilute hydrochloric acid of approximately half-normal strength was prepared, containing 1.196 grams codeine, $C_{18}H_{21}NO_3$, in 200 cc. The results obtained with this solution are given in Table III.

TABLE III.—EFFECT OF VARYING THE AMOUNT OF CODEINE ON THE CONSTANCY OF THE PROPORTION OF HCl IN THE ALKALOIDAL RESIDUE.

0.02 *M* codeine taken. cc.	0.1 *N* NaOH required. cc	0.1 *N* $AgNO_3$ required. cc.	Amount of HCl found. Milligrams.	Theory for $C_{18}H_{21}NO_3$.HCl. Milligrams.
5	0.70	1.00	3.54	3.54
10	1.35	2.00	7.09	7.09
20	2.85	3.96	14.04	14.18
30	4.40	5.96	21.13	21.27
40	5.90	8.00	28.36	28.36
50	7.40	9.98	35.38	35.45

Narcotine.—A 0.02 *M* solution of narcotine in dilute hydrochloric acid of approximately half-normal strength was prepared, containing 1.652 grams narcotine, $C_{22}H_{23}NO_7$, in 200 cc. The results obtained with this solution are given in Table IV.

TABLE IV.—EFFECT OF VARYING THE AMOUNT OF NARCOTINE ON THE CONSTANCY OF THE PROPORTION OF HCl IN THE ALKALOIDAL RESIDUE.

0.02 *M* narcotine taken. cc.	0.1 *N* NaOH required. cc.	0.1 *N* $AgNO_3$ required. cc.	Amount of HCl found. Milligrams	Theory for $C_{22}H_{23}NO_7$.HCl. Milligrams.
5	0.95	1.00	3.54	3.54
10	1.95	2.00	7.09	7.09
20	4.10	4.00	14.18	14.18
30	6.10	5.98	21.20	21.27
40	8.20	7.94	28.15	28.36
50	10.35	9.85	34.92	35.45

Atropine.—A 0.02 *M* solution of atropine in dilute hydrochloric acid of approximately half-normal strength was prepared, containing 1.156 grams atropine, $C_{17}H_{23}NO_3$, in 200 cc. The results obtained with this solution are given in Table V.

TABLE V.—EFFECT OF VARYING THE AMOUNT OF ATROPINE ON THE CONSTANCY OF THE PROPORTION OF HCl IN THE ALKALOIDAL RESIDUE.

0.02 *M* atropine taken. cc.	0.1 *N* NaOH required. cc.	0.1 *N* $AgNO_3$ required. cc.	Amount of HCl found. Milligrams.	Theory for $C_{17}H_{23}NO_3$.HCl. Milligrams.
5	0.10	1.02	3.62	3.54
10	0.20	2.00	7.09	7.09
20	0.80	4.00	14.18	14.18
30	1.10	5.96	21.13	21.27
40	3.60	8.02	28.43	28.36
50	5.30	9.85	34.92	35.45

Hydrastine.—A 0.02 *M* solution of hydrastine in dilute hydrochloric acid of approximately half-normal strength was prepared, containing

1.532 grams hydrastine, $C_{21}H_{21}NO_6$, in 200 cc. The results obtained with this solution are given in Table VI.

TABLE VI.—EFFECT OF VARYING THE AMOUNT OF HYDRASTINE ON THE CONSTANCY OF THE PROPORTION OF HCl IN THE ALKALOIDAL RESIDUE.

0.02 *M* hydrastine taken. cc.	0.1 *N* NaOH required. cc.	0.1 *N* $AgNO_3$ required. cc.	Amount of HCl found. Milligrams.	Theory for $C_{21}H_{21}NO_6.HCl$. Milligrams.
5	1.00	0.98	3.47	3.54
10	2.03	2.00	7.09	7.09
20	4.10	3.98	14.11	14.18
30	6.15	5.96	21.13	21.27
40	8.25	8.04	28.50	28.36
50	10.50	9.90	35.10	35.45

Pilocarpine.—A 0.02 *M* solution of pilocarpine in dilute hydrochloric acid of approximately half-normal strength was prepared, containing 0.832 gram pilocarpine, $C_{11}H_{16}N_2O_2$, in 200 cc. The results obtained with this solution are given in Table VII.

TABLE VII.—EFFECT OF VARYING THE AMOUNT OF PILOCARPINE ON THE CONSTANCY OF THE PROPORTION OF HCl IN THE ALKALOIDAL RESIDUE.

0.02 *M* pilocarpine taken. cc.	0.1 *N* NaOH required. cc.	0.1 *N* $AgNO_3$ required. cc.	Amount of HCl found. Milligrams.	Theory for $C_{11}H_{16}N_2O_2.HCl$. Milligrams.
5	0.98	1.00	3.54	3.54
10	1.95	2.00	7.09	7.09
20	3.85	4.00	14.18	14.18
30	5.90	6.02	21.34	21.27
40	7.90	8.10	28.71	28.36
50	9.95	10.15	35.98	35.45

Brucine.—A 0.02 *M* solution of brucine in dilute hydrochloric acid of approximately half-normal strength was prepared, containing 1.576 grams brucine, $C_{28}H_{26}N_2O_4$, in 200 cc. The results obtained with this solution are given in Table VIII.

TABLE VIII.

0.02 *M* brucine taken. cc.	0.1 *N* NaOH required. cc.	0.1 *N* $AgNO_3$ required. cc.	Amount of HCl found. Milligrams.	Theory for $C_{23}H_{26}N_2O_4.HCl$. Milligrams.
5	0.90	1.00	3.54	3.54
10	1.92	2.00	7.09	7.09
20	4.10	4.00	14.18	14.18
30	6.20	6.10	21.62	21.27
40	8.38	8.10	28.71	28.36
50	10.45	10.10	35.80	35.45

The results given in the accompanying tables show that at least fairly close results may always be obtained if we estimate the chlorine of the combined hydrochloric acid in the alkaloidal residue. It also appears probable that the application of the Volhard method to the estimation of alkaloids is limited only by the possible instability of the hydrochloride of the given alkaloid under the conditions adopted for getting rid of the excess of the uncombined acid. For estimating the actual amount of alkaloid in specimens of these alkaloids as obtained commercially or in the course of assay, we may therefore adopt the following procedure:

About 0.2 gram of the specimen to be examined is dissolved in an excess of dilute hydrochloric acid (about 20 cc. of 4 per cent.), the liquid completely evaporated on the water bath, the residue thoroughly stirred and mixed with 5 cc. of alcohol and the liquid again similarly evaporated. This treatment with 5 cc. of alcohol is repeated and the liquid again evaporated on the water bath. The residue is then taken up with distilled water (about 10 cc.), phenolphthalein added, and the acidity of the liquid titrated with standard alkali. This titration with alkali will in most cases indicate, at least approximately, the amount of hydrochloric acid that remained combined in the alkaloidal residue and hence may serve at least in indicating how much standard silver solution to add in the subsequent estimation of the chlorine by the Volhard method. Any precipitate formed on addition of the alkali is filtered off, washed with small amounts of water until a drop of the filtrate on testing with silver nitrate is shown to be free from chlorine. The filtrate is then diluted with distilled water to about 70 cc., acidified by adding 5 cc. of dilute (10 per cent.) nitric acid, and followed by a measured amount of standard silver nitrate solution which is judged to be a little in excess of that required to precipitate all the chlorine in the solution. The whole is then made up to definite volume (100 cc.) and filtered through a dry filter. To an aliquot portion (50 cc.) of the filtrate, 1 cc. of a 10 per cent. ferric alum solution is added, and the excess silver in the solution titrated with standard thiocyanate solution. Having determined the amount of hydrochloric acid and knowing that in the case of the alkaloids above mentioned 1 molecule of the hydrochloric acid is equivalent to 1 molecule of the alkaloid, we can of course calculate the actual amount of the latter in the specimen under examination. In the case of brucine, or in any other similar case where the color of the solution would interfere in determining the end reaction, an aliquot portion of the liquid may be evaporated to dryness on the water bath, the residue ignited, taken up with hot dilute nitric acid, and the excess silver in the solution titrated with standard thiocyanate in the usual way.

NEW BOOKS.

First Year Chemistry. By Wilhelm Segerblom, A.B., Instructor in Chemistry at the Philips Exeter Academy. The Exeter Book Publishing Company, Exeter, N. H. pp. xxv + 410. Price, $1.50.

This book is a departure from the ordinary textbook of chemistry, although a few others of its kind have recently appeared. It is essentially a laboratory outline containing directions for performing 169 experiments. Only about 75 pages are devoted to theoretical and general matters. Some descriptive material in fine print accompanies the experiments. The author states: "My plan is to use the inductive method rigorously in the first 90 experiments." The inductive method is then dropped and "is followed by the theory of chemistry, with experiments to illustrate the laws and principles; this comes at the middle of the year—a period now approved by many teachers. The theory of chemistry is followed by considerable descriptive chemistry, studied in the light of recent theoretical conceptions, but with the spirit of the inductive method still an unconscious guide. . . . . . My object has been to give the student a conception of chemistry from the point of view of the scholar and the thinker, rather than from the point of view of the crammer, *i. e.*, to teach *chemistry* rather than to teach *a text-book.*" This is all very well except that the average student falls somewhat short of the heights of the scholar and thinker, and, in the experience of the reviewer, he needs something more unified and systematic than the isolated observations derived from experiments in order to get a comprehensive idea of even elementary chemistry. The reviewer does not wish to disparage the inductive method, for it is most excellent when one has time for it and applies it judiciously in connection with a good text.

The experiments of the book before us are for the most part well selected, and the directions are clear and concise. The general outline, pp. 339–354, supplies a useful summary for the guidance of the scholar. The general method of treatment is, however, old-fashioned, as a few examples will show: Hydrate and hydroxide are employed interchangeably throughout, the author seemingly being unaware of the modern significance of the word hydrate. Bases are considered to be either metals, metallic oxides, or metallic hydroxides, pp. 317 and 344. The crude statements of Berthollet, p. 319, are overemphasized, while the subject of reversible reactions and chemical equilibrium receives but brief mention toward the close, p. 337, and it is only in the light of the latter that Berthollet's principles can be intelligibly treated. The method of treatment of molecular weights as derived according to Avogadro's hypothesis is inadequate, and molecular formulas of simple substances are used before any explanation of the reason therefor is given. All densities are referred to hydrogen as unity, and the whole subject is treated on the hydrogen basis instead of that of oxygen, as is the more modern custom. The conception of the gram-molecular-volume, which so simplifies this subject and also the solving of problems concerned with gas volumes, is not introduced at all.

Loose or inaccurate statements are not uncommon as for example, the definition of hydrolysis, p. 296, of acids, p. 343, and of combining number, p. 352, and the statement of Faraday's law, p. 332. Experiments like No. 102 do not give molecular weights, and there are a number of problems based upon it, p. 371. Among the examples of reduction pp. 341–2, under (4), only the action of copper upon nitric acid is commonly classed as reduction; and under (5) and (6) the reactions are simply dissociations. Experiment 168 does not give the amount of salt dissolved in 10 cc. of *water*, but the amount present in 10 cc. of the *solution*.

Simplified spelling is used in the case of a few words, as "tho" and "thru," without any attempt to carry out all of the recommendations of the Simplified Spelling Board. "Hight" occurs throughout instead of the more usual form "height."

The typography of the book is good, and the proof-reading was carefully done except on p. 324. The main divisions of the text on pp. 183, 219, and 265 are not well indicated. O. F. TOWER.

Anleitung zum Experimentieren in der Vorlesung über organische Chemie. Zum Gebrauche an Universitäten, technischen Hochschulen und höhere Lehranstalten, sowie zum Selbstunterricht für Studierende. DR HANS RUPE, a. o. Professor an der Universität Basel. Vieweg und Sohn: Braunschweig, 1909. pp. 130. Geheftet, Mk. 4.50; Lnwd, Mk. 5.40.

This is a collection of lecture experiments for those giving courses in elementary organic chemistry and, as indicated in the supplementary title, may also be used advantageously by the student as a laboratory guide in the preparation and study of organic compounds.

The experiments include the determination of carbon and hydrogen, of nitrogen and of molecular weights; the preparation and properties of a large number of typical carbon compounds illustrative of the more important groups and reactions, together with such other topics as the distillation of petroleum and of wood, illuminating and water gas, fermentation soap, candles, equilibrium in esterification, bread-baking, collodion and guncotton, and the like.

The selection of experiments is, on the whole, quite satisfactory, the material is well classified and arranged, and the descriptions generally clear and explicit. The preparation of such substances as mercury fulminate, nitroglycerol, zinc ethyl, and the like, is, however, fraught with too much danger to be commended for lecture room demonstration or for inclusion in a book to be used as a laboratory guide for beginners.

As every organic chemist well knows, the great handicap encountered in lecture demonstration in his chosen field is the length of time needed to carry out many of the most important reactions. Where this difficulty cannot readily be avoided, the author meets it either by showing in the lecture room only the final step in the reaction or by continuing the reaction through successive lecture periods. In reading over the description of the experiments, the inorganic chemist cannot fail to be impressed with the laborious and time-consuming character of many of them as compared with the numerous relatively simple and rapid ones available in his own field.

The book should prove useful to all teachers of organic chemistry.

MARSTON TAYLOR BOGERT.

Calculations of General Chemistry. WILLIAM J. HALE. New York: D. Van Nostrand Company. pp. 174. Price, $1.00.

This book is designed for use during the first year of the student's progress in the study of chemistry. It comprises the units of measure, and the calculations based on density and specific gravity; effect of pressure and temperature on gases; Avogadro's hypothesis; law of definite proportions; derivation of formulas; chemical equations; normal solutions; combination of gases by volume and closes with an appendix giving a table of logarithms. The treatment is clear and concise and the volume will be of service to students.

In the calculations of density the author uses oxygen as the standard. He says: "Formerly hydrogen, as the lightest substance served this purpose, and consequently the close relatiouship between densities and molecular weights was apparent. In recent times oxygen, with the value of 32, has been adopted as the basis of molecular weights by reason of the great importance of this element in its numerous combinations with other elements and for reasons that will be made clear after further considerations."

The reasons for making oxygen the standard for densities are no clearer than those for making it the standard for atomic weights. Hydrogen is the only standard that is rational and scientific and the use of oxygen as a standard leads the student to confusion only. It is unfortunate that, even among scientists, a fad or fancy promulgated by some man of prominence so often finds many eager followers. WM. L. DUDLEY.

An Introduction to Physical Science. By FREDERICK H. GETMAN. John Wiley & Sons, New York. 1909. Price, $1.50.

The author has written this little book to meet the difficulties of beginners in chemistry by giving, in logical order, the physical principles which are most important for an intelligent study of chemistry. Seventy-eight pages are devoted to mechanics, 35 of which are concerned with gases and liquids. Sixty pages are devoted to heat and thermodynamics, while light electricity and magnetism are considered in the remainder of the 250 pages. Each chapter is concluded with a number of good problems and questions. If a student were acquainted with the contents of this book he would be well prepared to take up a study of chemistry, but it is not plain just when there will be time to devote to a course of this kind, unless it is taken in lieu of the regular course in physics. This book raises an interesting question; namely, is it desirable to have the principles of physics given with a special view to the study of chemistry? There might seem to be some advantages in this from the standpoint of the teaching of chemistry. On the other hand, if the student is held strictly accountable for everything he has had in physics, rather than attempting to give it to him in a somewhat different way, he would frequently need to get out his physics and do some independent thinking in applying the principles to the new things presented to him. This would be a gain in many ways: it would emphasize the importance of thorough work for future use, it would give more time for things more strictly chemical and good students would not be bored with an elementary presentation of things with which they were already familiar. Wherever this method is possible it certainly would tend to develop more thinking by the student in chemistry, a point that is of first importance.

G. A. HULETT.

The First Principles of Chemical Theory. By C. H. MATHEWSON. John Wiley & Sons. pp. 123. Price, $1.00.

This book of 123 pages is used by the author as a supplementary text to a short course of lectures which follow the first four months' work in general chemistry. The purpose is to introduce the student to the principles of chemistry very early in his course with the idea of continually repeating and illustrating these principles as the student accumulates facts in his subsequent work. Besides the subjects generally touched upon in a course in general chemistry, the student is introduced to the subject of osmotic pressure and related phenomena, electrolytic dissociation theory, heterogeneous equilibrium, thermochemistry and the many terms and conceptions accompanying these subjects. When the student once gains a working knowledge of these things his work will become mentally interesting and very much more intelligible and profitable, so it is desirable to have these things as early in the course as possible. On the other hand, any real conception of these principles should be based on an intimate (laboratory) knowledge of some facts. Without this the principles are merely so many words and when introduced again the student remembers having heard about them, while on repetition he may come to dislike the subject and so lose the mental training and pleasure that should go with a study of chemistry. This unfortunate result is alltogether too frequently encountered in third- and fourth-year students, and it emphasizes the importance of determining just what basis of fact is necessary to afford a working conception of a given principle. The increasing favor of quantitative experiments in general chemistry laboratory work is an expression of this need, and it would seem that the rational development of the instruction in chemistry must give considerable attention to questions as to just when a particular principle is to be introduced so that it may stimulate the reasoning powers and be an effective tool in the further study. The compact statements in which the principles of chemistry are expressed afford rather poor material for a memory exercise. It would seem, therefore, to be desirable to develop the principles and theories, at least during the whole course of undergraduate chemistry, rather than in a single course of lectures. G. A. HULETT.

Elements of Mineralogy, Crystallography and Blowpipe Analysis, from a practical standpoint including a description of all common or useful minerals, the tests necessary for their identification, the recognition and measurements of their crystals, and a concise statement of their uses in the arts. By ALFRED J. MOSES and CHARLES LATHROP PARSONS. Fourth edition, vii + 444 pages, 580 figures and three double pages of tables for determinative mineralogy. New York: D. Van Nostrand Company. Price, $2.50.

The fourth edition of this well-known book differs but very slightly from the third edition (1904). Some changes in the introductory chapter, a few paragraphs added, and the statistics of production and value revised are the only changes noted. The main body of the text, descriptive of the mineral species, has not been changed. For instance, molybdite is still stated to be MoO_3 (page 277), and thorianite is not mentioned at all. While it is always difficult to decide on what to include and what to exclude from "all common or useful minerals," it would seem more desirable to include a mineral like dumortierite which has been found in this country in five different states, rather than such rare ones as aikinite, aphthitalite, etc. It must be somewhat confusing, particularly to a student, for whom the book is specially adapted, to find under pyroxene, crystal drawings of "fassaite" and "leucaugite" (Figs. 518 and 519), neither of which is mentioned in the text or in the index. The brief mention of many of the not very common yet still not very rare minerals would be a slight improvement on this otherwise excellent book, which gives, as the extended sub-title briefly indicates, about all the essential facts of mineralogy. W. T. SCHALLER.

Annuaire pour l'An 1910. Published by the Bureau des Longitudes. 16 mo., 820 pages. Paris: Gauthier-Villars, 1910. Price, 1.50 francs.

As cheap as before, as full of inaccuracies as usual. In the immense amount of information given upon astronomical, geographic, physical and chemical phenomena, the larger part is of course correct, but a short search brings to light so many inaccuracies that the work as a whole must bear the stigma of being unreliable, at least as regards physical and chemical data. In one place, a column of chemical equivalents of the elements is headed "electrochemical equivalents." In a table of atomic weights and chemical equivalents, antimony, arsenic, nitrogen, bismuth, boron, phosphorus and silicon are considered as *monovalent* elements, aluminium is bivalent (!), while vanadium with an atomic weight of 51.2 has an equivalent weight of 68.5 (!!). Inaccurate values determined by French experimenters are frequently given to the exclusion of greatly more accurate ones by non-Gallic scientists. As a scientific compilation, in the proper sense of the term *scientific*, it is discreditable to the authors and to France.

JOSEPH W. RICHARDS.

A System of Diet and Dietetics. Edited by G A. SUTHERLAND. London, 1908. xiii + 893 pp. Price, $7.50.

This volume, which is one of the series entitled Oxford Medical Publications, contains a number of papers by different authors on food and nutrition in health and disease. Among the papers of special interest to students of nutrition may be mentioned: "A Discussion of General Principles," by Sir Lauder Brunton; "The Evolution of Man's Diet," by Dr. Harry Campbell; "The Physiology of Digestion, Absorption, and Nutrition," by Dr. E. I. Spriggs; "The Results of Experimental Work on Diet," by Dr. E. I. Spriggs; "Diet Cures and Special Diets," by Dr. Edmund Cautley; "Patent and Proprietary Foods," by Dr Edmund Cautley; "Diet in Old Age," by Dr. Harry Campbell; and "The Feeding of Infants and Children in Health," by Dr. G. A. Sutherland.

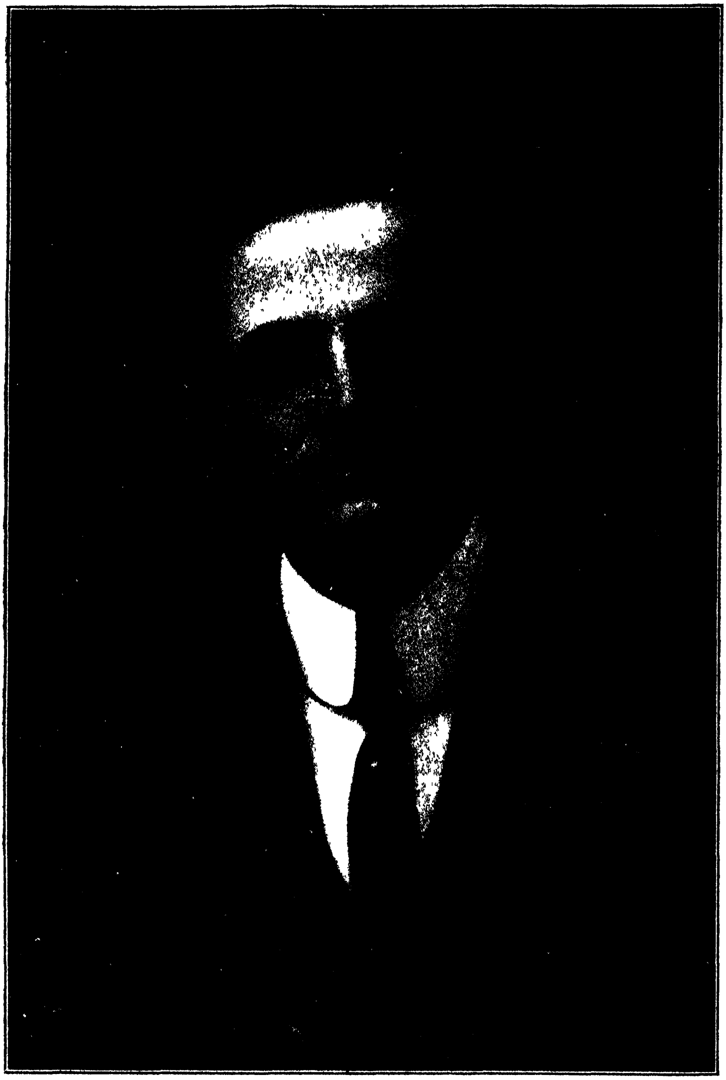
In the chapter on the Evolution of Man's Diet, the epochs which the discussion treats are: The simian period, the homo-simian period, the early hunting period, the pre-cibicultural cookery period, and the cibicultural period, or the period in which man has depended upon cultivated crops for food. Dr. Campbell has brought together a large amount of information not generally accessible and has rendered a service to all students of dietetics by the clear and systematic way in which the evolution of man's diet is discussed.

All the sections are of decided interest and value as they represent the views of men of wide experience in the subjects treated as well as summaries of data fundamental to adequate discussion of such questions. The chapters on diet in disease are of unusual interest to the medical practitioner. As stated in the editor's preface "this book is not a reflection of the fancies of the public on the subject of their food, or of the methods of the individual who believes in an infallible system for dieting of his patients. Until our knowledge of physiology is more perfect than at present the scientific basis of dietetics must be an unstable one. Nevertheless patients must be dieted, and the physician must be guided by the teaching of history, by experimental physiology, and by clinical experience in the proper regulation of their diet. All that has been attempted in this book is to set down the principles and practice of men who have had special experience in the subjects on which they write."

C. F. LANGWORTHY.

Die Methoden zur Herstellung Kolloider Lösungen Anorganischen Stoffe. By Dr. The. Svedberg. Published by Theodor Steinkopff, Dresden. 500 pp. 16 Marks, unbound.

This extensive work is confined to the methods of preparation and is not a general treatise on colloidal solutions. All known methods of inorganic colloid preparation are thoroughly and systematically treated. They are divided into condensation and dispersion methods. The former are again divided into reduction, oxidation, hydrolysis and other condensation methods. The latter are divided into mechanical-chemical and electrical dispersion methods. Each of these subdivisions is taken up separately and the descriptions are preceded by very complete literature references. Under the electrical dispersion method is given a well illustrated description of the author's improvement of Bredig's method. An oscillatory discharge with large electrical capacity produces the colloidal metal much more rapidly than does the application of the simple direct current, as described by Bredig. The book is a very complete treatment of the methods of preparation of inorganic colloids, and suggests the need of a similar separate treatise on organic colloids and one on properties and characteristics of colloids. W. R. Whitney.



W. R. Whitney

VOL. XXXII. FEBRUARY, 1910. No. 2.

THE JOURNAL

OF THE

American Chemical Society

SOME CHEMISTRY OF LIGHT.[1]

BY W. R. WHITNEY.

From the dawn of history, chemistry has had much to do with the production of artificial light, and I wish now to recall to your minds a few illustrations I will not burden your ears with a long story on physics or mechanics of light, but intend treating the subject of artificial light so as to show you that it has always been largely a subject for chemical investigation I want to impress upon your minds that it is still a most green and fertile field for the chemist. I have tried to arrange a few familiar experiments to illustrate some of the facts touched upon, and it should be borne in mind that I am trying to interest an audience of chemists from widely different fields, rather than to present a chronological record of recent experimental research.

I cannot tell just when chemistry was first scientifically applied to a study of artificial light. Most cardinal discoveries are made by accident and observation. The first artificial light was not made by design nor was the first improvement the result of chemical analysis. It is supposed that the first lamps were made from the skulls of animals, in which oil was burned. Herodotus, describing events about three centuries before Christ, says of the Egyptians: "At the times when they gather together at the city of Sais for their sacrifices, on a certain night they all kindle lamps many in number in the open air round about the houses; now the lamps are saucers full of salt and oil mixed and the wick floats of itself on the surface and this burns during the whole night." This night was observed all over Egypt by the general lighting of lamps, and these lamps were probably the forerunners of the well-known Greek and Roman lamps of clay and of metal which are so common in our museums.

---

[1] Presidential address delivered at the Boston Meeting of the American Chemical Society, December 29, 1909.

The candle and lamp were probably invented very much earlier. We know that both lamps and candles were used by the priests of the Jewish temple as early as 900 B. C. The light of those candles and lamps was due, as you know, to particles of carbon heated in a burning gas.

It is not fair to the chemists of our early candle-light to skip the fact that great chemical advances were made while candles were the source of light, and so I touch for a moment upon one of the early applications of chemical knowledge. The fats and waxes first used were greasy and the light was smoky and dull. They were capable of improvement and so the following chemical processes were developed and applied to the fats. They were first treated with lime, to separate the glycerol and produce a calcium soap. This was then treated with sulphuric acid, and the free stearic and palmitic acids separated. These acids were then made into candles and gave a much whiter light than those containing the glycerol ester previously used. Similar applications of chemical principles are probably known to you all in the refining of petroleum. The crude distillate from the rock oil is agitated with sulphuric acid and then washed with a solution of sodium hydroxide. This fact accounts, in considerable degree, for the advance of a number of other chemical processes. An oil refinery usually required the presence of a sulphuric acid plant in the immediate vicinity, and this often became a source of supply for other new chemical industries.

Very great advances have been made in the use of fats and oils for lighting purposes, but there is so much of greater interest in later discoveries that we will not consider many of them. The distillation of gas from coal or wood in 1739 was a chemical triumph, and a visit to a gas plant still forms one of the main attractions to the young chemist in an elementary course of applied chemistry. The first municipal gas plant was established in London, just about 100 years ago. The general plan, so apparently simple to us to-day, was at its inception judged impracticable by engineers. In spite of other methods of illumination, the improvements in the making, purification and application of illuminating gas have caused a steady increase in its use. Gas owes its illuminating power to the fact that a part of the carbon in it is heated to incandescence during the combustion of the gas. It must contain, therefore, such carbon compounds as yield a fair excess of carbon, and this knowledge has led to the schemes for the enrichment of gas and for the use of non-luminous water-gas as a base for illuminating gas.

Various schemes were devised in the early part of the 19th century for using gas to heat to incandescence, rods or surfaces of lime, zirconia and platinum. This was not at first very successful, owing to imperfect combustion of the gas. The discovery of the Bunsen-burner principle was made a little later. By thus giving a much higher temperature to the gas flame and insuring complete combustion, this gave new impetus to this branch, and the development of suitably supported oxide mantles continued for half a century.

Most prominent in this field is the work of Auer von Welsbach. It was a wonderful series of experiments which put the group of rare-earth oxides into practical use and started a line of investigation which is still going on. The Welsbach mantle practically substitutes for the carbon of the simple gas flame, another solid in a finely divided shape capable of giving more efficient light. This allows all of the carbon of the gas to contribute to the production of a hotter flame. But more interesting than the mechanical success, to my mind, is the unforeseen or scientifically unexpected discovery of the effect of chemical composition. By experiment it was discovered that the intensity and color of the various mixtures of difficultly fusible oxides at incandescence varied over a wide range. Thus a broad field for unforeseen investigation was opened. The samples of Welsbach mantles which you see before you were kindly loaned to me by Mr. H. S. Miner, of the Welsbach Company, and beautifully illustrate the application of advanced chemical work to this industry. The color and intensity of the light varies in an unexplained manner with slight differences in composition of the mantle. The following are the composition and candle powers of the mantles shown:

CANDLE POWER OF MANTLES, RANGING FROM PURE THORIA TO 10 %CERIA.

No.	Per cent. thoria.	Per cent. ceria.	Candle power.
367	100.00	0.00	7
368	99.75	0.25	56
369	99.50	0.50	77
370	99.25	0.75	85
371	99.00	1.00	88
372	98.50	1.50	79
373	98 00	2.00	75
374	97.00	3.00	65
375	95.00	5.00	44
376	90.00	10.00	20
69		La, Zr, Ce, oxides,	30

The methods of making present mantles were also a part of Dr. Auer's contribution to the art. Suitably woven fabrics are dipped into solutions of the rare-earth salts; these are dried and the organic matter burned out, leaving a structure of the metal oxides.

The pure thoria gives a relatively poor light. The addition of the ceria, up to a certain amount, increases the light. This added component is called the "excitant," and as the cause for this beneficial action of the excitant is not known, it is possible that further discoveries along this line will yet be made. There is hardly a prettier field for chemical speculation than is disclosed by the data on these light efficiencies. For some unknown reason, the change in composition by as little as one per cent. varies the luminosity over tenfold, and yet, more than one per cent. of the excitant (ceria) reduces the light. Besides the temptation to speculation, such disclosures of Nature encourage us to put greater trust in the value of new experiments, even when accumulated knowledge does not yield a blazed trail for the pioneer. By giving a discovery a name and attaching to it a mind-quieting theory, we are apt to close avenues of advance. Calling this small amount of ceria an "excitant" and guessing how it operates, is directly harmful unless our guess suggests trial of other substances.

One of the explanations proposed to cover the action of the ceria ought to be mentioned, because it involves catalysis. This is a term without which no chemical lecture is complete. Some think that the special mantle mixture causes a more rapid and localized combustion and therefore higher temperature, by condensation of gas in its material. Others think that this particular mixture permits of especially easy and rapid oxidation and reduction of its metal oxides themselves in the burning gas mixture. The power which catalyzers have of existing in two or more states of oxidation seems to apply also to the ceria of the Welsbach mantle. Whatever the truth may be, it has been shown by Swinton[1] that when similar oxide mantles are heated to incandescence by cathode rays *in vacuo*, the presence of one per cent. ceria produces only a very small increase in the luminosity of thoria. It is interesting to note that in the gas flame pure ceria gives about the same light as pure thoria, while in the cathode rays of the Crookes tube, with conditions under which ceria gave almost no light, pure thoria gave an intense white light. These facts, which are still unexplained, illustrate how little is understood in this field.

I will merely refer to the fact that vapors of gasoline, kerosene, alcohol, etc., are also now used in conjunction with the Welsbach mantles.

The field of acetylene I must also omit with a mere reference to the fact that the manufacture of calcium carbide was a chemical discovery and the action of water upon it, producing the brilliantly-burning acetylene gas, was another.

Turning now to electrical methods of generating light, we find the chemist early at work. Sir Humphry Davy and others, at the dawn of the 19th century, showed possibilities which since that time have been developed into our various types of incandescent and arc lamps. We naturally attach Mr. Edison's name to the development of the carbon incandescent lamp, because it was through his indefatigable efforts that a practicable lamp and illuminating system were both developed. It had long been known that platinum, heated by the current, gave a fair light, but it melted too easily. A truly enormous amount of work was done in attempts to raise the melting-point of the platinum, and the effect of occluded gases, of annealing, of crystalline condition, etc., etc., were most carefully studied, but the results were unsatisfactory. He was therefore led to the element carbon as the next most promising conductor of high melting point. Edison's persistent and finally successful attempt to get a dense, strong, practical filament of pure carbon for his lamps, is one of the most encouraging lessons to the chemist of to-day. This history needs to be read in the light of the knowledge of carbon at that time and the severe requirements of a commercially useful carbon filament. It illustrates the value of continued effort when it is based on knowledge or sound reasoning. The search was not the groping in the dark that some of us have imagined, but was a resourceful search for the most satisfactory, among a multitude of possible materials. From our point of view, all subsequent changes in choice of material for incandescent lamp filaments have been indicated by the knowledge that high melting point and low vapor-tension were the first requirements. If you will consult the curve of the *melting points* of all the *elements*, as plotted against their *atomic weights*, you will see at once that the desired property of high melting point is a periodic functionof the atomic weight. And it is this fact, which was independently disclosed as a general law by Meyer and Mendeléeff, in 1863, that has aided in the selection of all the new materials for this use. You will notice that the peaks of the curves are occupied by such elements as carbon, tantalum, tungsten, osmium, etc., which are all lamp materials.

---

[1] *Proc. Roy. Soc., London* (*A*), 65, 115.

A study of the laws of *radiation* also soon played a part in incandescent lamp work. The early rough and black filament of bamboo was first replaced by a polished black carbon filament, and later by one which had a bright, silver-gray coat of graphite. A black body at any temperature radiates the maximum possible energy in all wave lengths. Heated to incandescence, it will *radiate more invisible and useless infra-red rays than any other* opaque material at the same temperature. A polished metal is therefore a more efficient light source than the same metal with a black, or even rough surface. This is derived from Kirchoff's Law of Radiation and Absorption, which was early established.

It may seem like penetrating too far into detail to consider for a moment the changes in structure and surface which the carbon filament of our incandescent lamps has undergone, but the development of such an apparently closed problem is instructive because it has yielded to such simple methods of attack. The core, or body, of the carbon filament of to-day is made by some one of the processes based on dissolving and reprecipitating cellulose, such as are used in artificial silk manufacture. The cellulose solution is squirted through a die into a liquid which hardens it into dense fibers. These cellulose fibers are then carbonized by being heated, out of contact with the air, at as high a temperature as possible with gas furnaces. All of this is also merely the application of chemistry which was first worked out in some of the German chemical laboratories. This plain carbon filament, the result of this simple process which might have been satisfactory in the early days, would be nowadays useless in a lamp, as its practical life is only about 100 hours at 3 watts per candle. In a subsequent process of manufacture it is therefore covered with a steel-gray coating of graphite, which greatly improves the light-emitting power. This coat is produced by heating the filament in an atmosphere of benzene or similar hydrocarbons. The electric current which heats the filament is of such an intensity that the decomposition of the hydrocarbon produces a smooth, dense deposit of graphite. With this graphite coat the filament now burns about 500 hours; but the simple graphite coat can itself be improved. It is improved by being subjected, for a few moments, in the electric furnace, to a temperature of about 3500°, so that the life now becomes about 1500 hours under the same operating conditions as before. The product of this treatment is known as the metallized filament, because its temperature coefficient of resistance is by this last step made similar to that of the metals.

A case is shown on the table which contains illustrations of the carbon incandescent lamp manufacture in the shape of cellulose solution, squirted cellulose fiber, carbonized fiber, etc.

Among the incandescent lamps which are before you I have one containing a platinum wire filament. You will see, as I turn on the current, that the intensity of its light is not very great, even when the current is sufficient to melt the wire. A much greater luminosity is produced by a plain carbon filament, and a still greater by the graphite coated and metallized carbon before they are destroyed. In the case of carbon, the useful life of the lamp depends much more on the vaporization of the material than on its melting point, and these lamps, as shown, will operate for a short time at very much greater efficiencies or higher temperatures than is possible when a practical length of life is considered. Thus, besides the physical effect of surface quality, we have evidence of differences in the vapor pressure of different kinds of carbon. It looks as though carbonized organic matter yielded a carbon of much greater vapor pressure for given temperature than graphite, and that even graphite and metallized graphite are of quite distinctly different vapor pressures at high temperatures. It may be interesting to note here that if the carbon filament could withstand for 500 hours the maximum temperature which it withstands for a few moments, as shown in the experiments, then the cost of operating incandescent lamps could be reduced to nearly a fifth of the present cost.

It was discovered by Auer von Welsbach that the metal osmium could be made into a filament, though it could not be drawn as a wire. The osmium lamp was the first of the recent trio of metallic filament incandescent lamps. The tantalum lamp, in which another high melting point metal replaces the superior but more expensive osmium, has been in use six or eight years. This surpasses the carbon in its action, and on running up to its melting-point it shows still brighter light than carbon. More recently the tungsten filament lamp has started to displace both lamps. At present this is the element which withstands the highest temperature without melting or vaporizing, and on being forced to its highest efficiency in a lamp you see that it reaches higher luminosity and that there is a similarity to carbon and tantalum in that an enormously greater efficiency may be produced for a very short time than can be utilized for a suitable length of life. The inherent changes at these temperatures, distillation or whatever they are, quickly destroy the lamp. The lamp will burn an appreciable time at an efficiency fifteen times as great as that of the common operating carbon incandescent lamp (at 3 watts per candle). In other words, light may be produced for a short time at an energy-cost one-fifteenth of common practice, so that there is still a great field for further investigation directed towards merely making stationary those changing conditions which exist in the burning lamp.

While it is generally true that the light given by a heated body increases very rapidly with rise of temperature above 600°, the regularity of the phenomenon is commonly overestimated. A certain simple law covering the relation between the temperature and the light emitted, has been found to apply to what we have called a black body. This so-called Stefan-Boltzmann law states that "the total intensity of emission of a black body is proportional to the fourth power of the absolute temperature." There are, however, very few real black bodies in the sense of the law. The total emission from a hole in the wall of a heated sphere has been shown experimentally to follow the law rigidly,* but most actual forms and sources of illumination do not. Most practical sources of artificial light are more efficient light producers than the simple law requires. This may be said to be due to the fact that these substances have characteristic powers of emitting relatively more useful energy as light than energy of longer wave length (or heat rays). Most substances show a power of selective emission and we might say that an untried substance, heated to a temperature where it should be luminous, could exhibit almost any conceivable light effect. It is still less possible to predetermine the proportionality between luminous and nonluminous emission. A simple illustration will serve to make this clear: if a piece of glass be heated to 600°, it does not emit light. If some powder such as zirconia or thoria be sprinkled upon it, light is emitted and the proportion of light at the same temperature will depend upon the composition of the powder. Coblentz has shown, both for the Auer mantle and for the Nernst glower, that the emission spectra are really series emission bands in that portion of the energy curve which represents the larger part of the emitted energy. This is in the invisible infra-red part, and so the laws which govern the emission at a given temperature depend upon the chemical composition of the radiant source. Silicates, oxides etc., show characteristic emission bands.

One of the most attractive fields of artificial light production has long been that of luminous gases or vapors. It has seemed as though this ought to be a most satisfactory method. The so-called Geissler tubes in which light is produced by the electrical discharge through gases at low pressure are familiar to all. The distribution of the energy emitted from gases is still further removed than that of solids from the laws of a black body, and a large proportion of the total electrical energy supplied to a rarefied gas may be emitted as lines and bands which are within the range of the visible spectrum. These lines, under definite conditions of pressure, etc., are characteristic of the different elements and compounds. The best known attempts to utilize this principle are the Moore system of lighting, in which long tubes of luminous gas are employed, and the mercury lamps, which, while more flexible on account of size, are still objectionable because of the color of the light. A simple form of mercury arc is shown.

It is rather interesting that the efficiencies of all of these various sources of electric light are not nearly so widely different as one would expect from a consideration of the widely divergent methods of light production employed.

From the light of a vapor or gas to that of an open arc is not a wide step, but the conditions in the arc are apparently quite complex and there is a great deal of room for interesting speculation in the phenomena of an arc. Briefly, there are two kinds of arcs to be considered in lighting. One has been in use for a century, the other for a few years only. The first is the successor to Sir Humphry Davy's historical arc between charcoal points. In this kind of arc the current path itself is hardly luminous and the light of the lamp is that given by the heated electrodes. In case of direct current it is the anode, or positive electrode, which gets the hotter and gives far the greater part of the light. In the carbon arc shown, it will readily be seen that the light is emitted by the heated solid carbon of one electrode. This gives a steady source of light, but is not so efficient as an arc in which material in the arc stream itself is the source of light. The arc may be made to play upon rare earth oxides, and these, being heated to incandescence, increase the luminosity, but this has not proved useful. The more common way is to introduce into the carbon electrode certain salts which volatilize into the arc and give a luminous effect. Here cerium fluoride, calcium fluoride, etc., are used, and the color of the arc, just as in the case of gas mantles, may be varied by varying the composition of the electrodes. This is seen in the arc from the carbon electrodes containing such salts.

I have arranged several different kinds of arcs and before each is a magnifying lens, to throw the image of the arc upon a screen. This permits our seeing the phenomena of the arcs and observing the characteristics of each. The very essential difference between the plain carbon arc and the luminous or flaming arc is readily noticed. In the latter case the greater part of the light is due to the incandescent metallic vapors in the space between the electrodes. Substitution of one chemical for another in such flaming arc electrodes has covered quite a wide range of chemical investigation. Salts are chosen which give the greatest luminosity without causing the formation of too much ash or slag. Some compounds of calcium, for example, are practicable, while others are not, though all of these would, under suitable conditions, yield the calcium spectrum.

If such salts as calcium fluoride were conductors at ordinary temperature, useful electrodes for flame arcs would probably be made from them. Such conducting materials as iron oxide, carbides, etc., have been used for flame arc electrodes, and a great many of the so-called magnetite arcs are now in use. The electrodes in this case are largely magnetic oxide of iron, with such other ingredients as titanium and chromium oxides, to increase the intensity of light, to raise the melting point of the mixture, etc.

As will be seen from observing this arc, the light is very white and intense and is generated by the heated vapors of the arc proper. A great many modifications of this arc principle are possible. Titanium carbide and similar substances give characteristic arcs, and some of them are very intense and efficient. For purposes of comparison, I have added to this illustrating experiment an arc of titanium carbide and one of copper.

The Nernst Lamp.

A distinct species of electric incandescent lamp is that invented about 10 years ago by the well-known physical chemist, Professor Nernst. This employs for filaments a class of bodies which are not electrical conductors at all at ordinary temperatures, and which, at their burning temperatures, do not conduct the current as metals and carbon, but as a solution does. This kind of conductivity, the electrolytic, involves electrochemical decomposition at the electrodes, and in the case of the Nernst filaments these otherwise destructive reactions are rendered harmless by the continual oxidizing action of the air. For this reason this type of lamp will not burn *in vacuo*. For its most perfect utility the principle of the Nernst lamp seems to require a mixture of oxides, because a single one is not so good a conductor nor so luminous. It uses oxides because these are the most stable compounds known, and it uses the rare-earth oxides because they have higher melting points than other oxides. As the efficiency very rapidly rises with the temperature, there is a great advantage in using the most infusible base possible. For that reason, zirconia, thoria, etc., are usually employed.

In this lamp a rod or filament of an oxide mixture, much like those used in Welsbach mantles, is heated by the current externally applied until it reaches a temperature at which it becomes a good conductor itself. Here again the peculiar laws of light radiation are illustrated, the light emitted at a given temperature being determined by the nature of the substance. Just as the pure thoria gives a poor light compared to the mixture with one per cent. ceria, so a pure zirconia rod, heated by the current, gives much less light than a rod containing a little thoria, ceria or similar oxide.

Work done by Coblentz on the energy-emission of such rods shows the emission spectra, at least in the infra red, to vary with the nature of the substance. In general, the spectra are not continuous like the spectra of metals and black bodies, but seem to occupy an intermediate position between these and luminous gases, which we know have usually distinct line spectra.

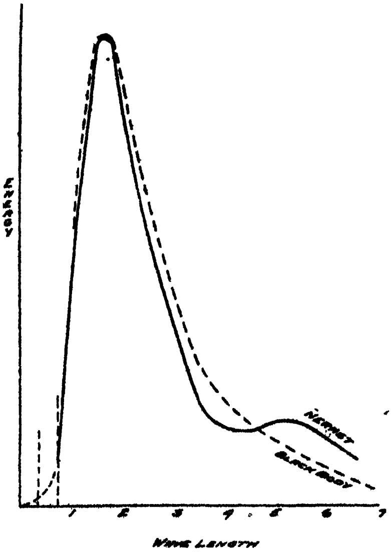


Fig. 1.

This recalls the subject of selective emission. Coblentz has shown selective emission in the long wave lengths for a Nernst glower. This is shown in comparison with the emission of a black body, in curve Fig. 1. The two sources, when compared at the temperatures where they exhibit the same wave length for maximum emission, differ very considerably in emission in the infra red, the black body giving more energy at the blue end, and less at the red end of the spectrum.

This is still more noticeable in the curves for such substances as porcelain, magnesia and glass, as shown by Coblentz's curves (Fig. 2).

The curves of wave length and radiant energy which are shown are, with slight modifications, taken from work of Lummer and Pringsheim and of Dr. Coblentz. The curve for the ideal, or black-body radiator, gives a picture of the total energy and its distribution over the different wave lengths. It is the peculiarity of the black body to radiate more energy of any given wave length than does any other body at the same temperature. Therefore, in case of all substances acting as thermal radiators, the black body will always give the greatest brilliancy. Since this body at the same time radiates a maximum in *all* wave lengths, it will be surpassed in light *efficiency* by any substance which is a relatively poor radiator in the invisible or non-luminous part of the spectrum.

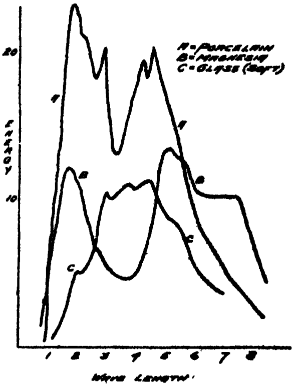


Fig. 2.

In the energy curves shown it is to be noticed that the visible part of the energy is practically only that between 0.4 and 0.8 thousandths of a millimeter. Consider the black lines in Fig. 3 for a moment. These show the emission of a black body at centigrade temperatures noted on the curves. Evidently the energy emitted rises very rapidly with the temperature; *i. e.*, as the 4th power of the absolute temperature. It will be noted also that the point of maximum energy or wave length corresponding to maximum energy shifts gradually toward the left or towards the visible wave lengths.

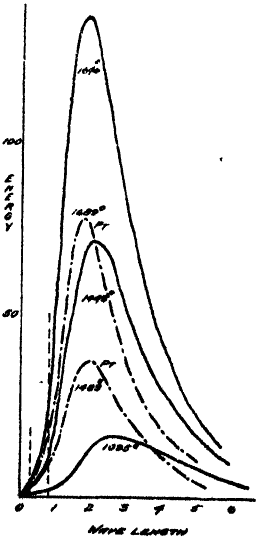


Fig. 3.

It is this rapid shifting of the position of maximum energy which makes the search for substances which can withstand even only slightly higher temperatures, of such great interest.

The curves for the black body and for platinum (dotted lines, Fig. 3), are not greatly different in general appearance, but the total amount of energy emitted at a given temperature from the black body is shown to be more than for the platinum, and it can be seen that at about the same temperature the platinum is the more economical light source. Prof. Lummer has said that at red heat, bright platinum does not radiate *one-tenth* the total energy which the ideal black body radiates at the same temperature, and at the highest temperature still less than one-half. The deviation of platinum from the black body law is a step in the direction of getting improved light-efficiency without corresponding increase of temperature. This method is practically without limit in its extension, for there seems to be no limit to the forms of energy curves which different substances may possess. The curves are apparently determined not only by physical state, but also by the chemical composition of the emitting substance.

You see before you a vacuum incandescent lamp which contains a ribbon of platinum, in the shape of a loop. While the section of the platinum is the same throughout, one-half of the loop is blackened by depositing a little platinum black upon it. This greatly affects the light efficiency as shown. The blackened portion, being more nearly a black body, radiates at each temperature relatively more energy of long wave length (*i. e.*, heat) than the bright portion; so for about equal total energy radiated the ribbon radiates less as light from the blackened surface.

In the production of artificial light, the tendency will always be in the direction of increasing the practical efficiency; *i. e.*, reducing the cost of light. We have seen that there is still much room for this. In the case of the kerosene oil lamps we know that much less than one per cent. of the energy of combustion of the oil is radiated as light from the flame. In the case of the most efficient source, the electric incandescent lamp at highest efficiency, we are still far from ideal efficiency. A still higher temperature would yield a yet higher efficiency. We do not know exactly how much light might possibly be yielded for a given consumption of energy, but one experimenter concludes that it is about ten candles per watt. If this is true, even the most efficient light you have seen this evening is less than half as efficient as it might be. Fortunately, it is not now clear just how the chemist is to realize all the advances which he will make in more efficient lights.

No consideration of this part of the subject is complete without a brief reference to the efficiency of the firefly. The source of his illumination is evidently chemical. This much is known about the process.

The light-giving reaction is made to cease by the removal of the air, and to increase in intensity by presence of pure oxygen. It is extinguished in irrespirable gases, but persists in air some time after the death of the insect. Its production is accompanied by the formation of carbon dioxide. These all indicate a chemical combustion process. Prof. Langley has shown that such a flame as the candle produces several

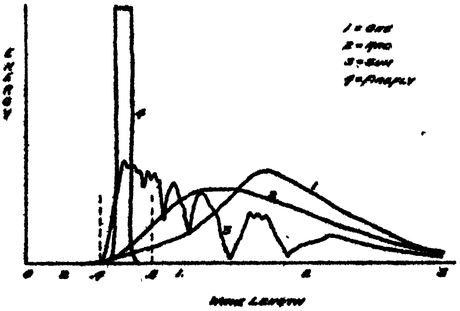


Fig. 4.

hundred times as muchus eless heat as the total radiation of the firefly for equal luminosity. In other words, the firefly is the most efficient light source known. This is illustrated by the energy distribution curves from several light sources taken from Prof. Langley's work (Fig. 4). The difficulties attendant upon the accurate determination of the curve for the firefly are so great that we ought not to expect very great accuracy in this case. These curves, which in each case refer to the energy after passing through glass, which cuts off energy of long wave lengths, represent the same quantities of radiant energy. While the sun is much more efficient than the gas flame or carbon arc, it still presents far the largest part of its energy in the invisible long wave lengths (above 0.8), while the firefly seems to have its radiant energy confined to a narrow part of the visible spectrum.

GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 46.]

THE HYDROLYSIS OF AMMONIUM ACETATE AND THE IONIZATION OF WATER AT HIGH TEMPERATURES.

BY A. A. NOYES, YOGORO KATO AND R. B. SOSMAN.

Received November 30, 1909

Contents.

1. Outline of the Investigation. 2. Apparatus and Method of Procedure. 3 Equivalent Conductance of Ammonium Chloride and Sodium Acetate. 4. Equivalent Conductance at Zero Concentration of the Various Substances. 5. The Equivalent Conductance of Ammonium Hydroxide and Acetic Acid. 6. The Ionization of Ammonium Hydroxide and Acetic Acid 7. Conductance of Ammonium Acetate Solutions at 18, 100, and 156°. 8. Hydrolysis of Ammonium Acetate and Ionization of Water at 100 and 156°. 9. Conductance of Ammonium Acetate Solutions at 18, 218, and 306°. 10. Hydrolysis of Ammonium Acetate and Ionization of Water at 218 and 306°. 11. Summary of the Results on the Hydrolysis of Ammonium Acetate and on the Ionization of Water, Ammonium Hydroxide, and Acetic Acid.

1. Outline of the Investigation.

In a paper from this laboratory published six years ago[1] an apparatus and method were described by which accurate measurements of the electrical conductivity of aqueous solutions could be made at temperatures up to 306°. In a second paper[2] were presented the results of the measurements of the conductivity of aqueous solutions of various salts, bases, and acids, and the ionization relations of these substances were discussed. The purpose of the research to be described in this article was to study another phenomenon—that of the hydrolysis of salts into

[1] THIS JOURNAL, 26, 134–170 (1904).

[2] *Ibid.*, 30, 335–352 (1908).

free acid and base—by measuring the change of conductance produced by adding an excess of the weak acid or base. Since the degree of hydrolysis is dependent on the degree of ionization of the water, this important quantity can be computed from it, when the knowledge of the hydrolysis is supplemented by that of the ionization of the acid and base involved. In this research there have been made measurements of the hydrolysis of ammonium acetate and of the ionization of ammonium hydroxide and acetic acid at temperatures of 100, 156, 218, and 306°.

The method employed for determining the hydrolysis is in principle that described first by Walker,[1] and later in more exact form by Bredig.[2] It consists in measuring the change in conductance produced by adding to the salt solution, in which the salt is partially hydrolyzed, a sufficient quantity of the slightly ionized acid or base to reduce the hydrolysis appreciably, and in computing, from the change produced by different quantities of acid or base added, the degree of hydrolysis. In this case it was practicable to reduce the hydrolysis by the addition of an excess both of the acid and of the base, since both are only slightly conducting substances; and in this case there results an increase in conductance corresponding almost exactly to that of the new quantity of ammonium acetate produced out of the free acid and base originally present.

The calculation of the ionization constant of water from the hydrolysis of the salt involves, as stated, a knowledge of the ionization constants of the acid and base. The determination of the former quantity therefore involves measurements of the conductance at various concentrations of solutions of the following substances; ammonium acetate; ammonium acetate with varying proportions of ammonium hydroxide and of acetic acid; ammonium hydroxide; acetic acid; ammonium chloride; sodium acetate; sodium chloride; sodium hydroxide; and hydrochloric acid. Measurements with dilute solutions of the last five substances are needed for the computation of the equivalent conductance at zero concentration of ammonium hydroxide and acetic acid. The results of such measurements with the last three substances have been previously published in THIS JOURNAL. The data for ammonium chloride and sodium acetate will be presented in this article.

2. Apparatus and Method of Procedure.

The conductivity cell used was like that previously described.[3] It consisted of a platinum-lined steel bomb, through the bottom of which passed a platinum electrode insulated from the bomb by being supported upon a quartz cylinder or by being contained in a quartz cup.

---

[1] *Z. physik. Chem.*, 4, 333 (1889).

[2] *Ibid.*, 13, 214–321 (1894).

[3] THIS JOURNAL, 26, 135–141 (1904).

The method of making the measurements was also in general similar to that followed in the previous researches in this laboratory. For a full description of the experimental procedure, of the preparation of the substances and analysis of the solutions, of the corrections applied for the conductance of the water and for contamination, and of all other experimental details, and also for a record of the original observations, the reader is referred to the more complete publication of this work which has been issued by the Carnegie Institution of Washington.[1] In this briefer article only the final results and the computations and conclusions based upon them will be presented.

3. Equivalent Conductance of Ammonium Chloride and Sodium Acetate.

Since ammonium chloride and sodium acetate are appreciably hydrolyzed at high temperatures (thus in 0.01 normal solution about 1.6 per cent. at 218° and 3.4–4.1 per cent. at 306°), the conductance of these salts was measured (except at 18 and 25°) in the presence of a greater or less proportion of ammonium hydroxide or of acetic acid;[2] and from the result was subtracted the conductance of the base or acid calculated from the ionization constants (given in Section 6) with the aid of the mass-action relations, $C_{OH} = K_B.C_{NH_4OH}/C_{NH_4}$ and $C_H = K_A C_{HAc}/C_{Ac}$. The measurements with ammonium chloride at 18, 100, and 156° were made by Prof. Yogoro Kato; at 18, 25, 218, 306° by Dr. R. B. Sosman; those with sodium acetate were made at 18, 100, 156 and 218° by Dr. H. C. Cooper;[3] and at 306° by Dr. R. B. Sosman.

Table 1 contains the final values derived from all these measurements by correcting the observed data for all known sources of error, so that they represent only the conductance of the pure unhydrolyzed salts. The concentration given in the second column represents the number of milli-equivalents of salt contained in one liter of solution at the temperatures corresponding to the conductance values given in the following columns. The latter are expressed in reciprocal ohms. In regard to the values at zero concentration see the next section. The temperatures are those on the hydrogen-gas scale (based at 218 and 306° upon the results of Jaquerod and Wassmer[4]).

---

[1] Publication No. 63 of the Carnegie Institution of Washington entitled "The Electrical Conductivity of Aqueous Solutions" This monograph may be obtained from the Institution at the rate of $2.50 per copy. The work with which this article is directly concerned will be found in Parts VI and VII of the publication.

[2] The ratio of NH_4OH to NH_4Cl in equivalents was 0.1 at 100 and 156°, about 0.5 at 218° and 1.0 to 4.6 at 306°. The ratio of $HC_2H_3O_2$ to $NaC_2H_3O_2$ was about 0.2–0.6 at 156 and 218° and 1.1 to 4.1 at 306°.

[3] These have been already published in This Journal, 30, 306, but are included here for the sake of completeness.

[4] *J. chim. phys.*, 2, 52 (1904).

TABLE I.—THE EQUIVALENT CONDUCTANCE OF AMMONIUM CHLORIDE AND SODIUM ACETATE.

Substance.	Concentration.	18°.	25°.	100°.	156°.	218°.	306°.
NH_4Cl	0	130.9	152.0	415	628	841	1176
	2	126.5[1]	146.5	399	601	801	1031
	10	122.5	141.7	382	570	758	925
	12.5	121.5	...	379	567	..	..
	30	118.1	...	...	..	..	828
$NaC_2H_3O_2$	0	78.1	...	285	450	660	924
	2	74.6	...	267.6	421	578	801
	10	71.2	...	253.3	396	542	702
	30	...	...	...	..	..	613
	80	63.4	...	221.0	340	452	..

4. Equivalent Conductance at Zero Concentration of the Various Substances.

The values of the equivalent conductance (Λ_0) at zero concentration for ammonium chloride and sodium acetate were obtained by extrapolation with the aid of the equation $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$. This when written in the form $1/\Lambda = 1/\Lambda_0 + K_1(C\Lambda)^{n-1}$ may be conveniently employed graphically by plotting $1/\Lambda$ against $(C\Lambda)^{n-1}$, the exponent $n - 1$ being taken equal to that value in the neighborhood of 0.5 which is found by trial to give most nearly a straight-line graph.[2] The values of Λ_0 for these two substances, already given in Table 1, are reproduced in Table 2, together with those previously determined for the various other substances which are needed in calculating the values of Λ_0 for ammonium hydroxide and acetic acid by means of the relations:

$$\Lambda_0(NH_4OH) = \Lambda_0(NH_4Cl) + \Lambda_0(NaOH) - \Lambda_0(NaCl)$$

$$\Lambda_0(HC_2H_3O_2) = \Lambda_0(NaC_2H_3O_2) + \Lambda_0(HCl) - \Lambda_0(NaCl).$$

The determinations of Λ_0 for sodium chloride, hydrochloric acid, and sodium hydroxide (up to 156°) have been previously described in THIS JOURNAL.[3] The value for sodium hydroxide at 218 and at 306°, where no measurements or no sufficiently accurate measurements exist, was derived under the assumption that it lies at such a proportional distance between the Λ_0 values for sodium chloride and hydrochloric acid at these temperatures as is indicated by its position between them at the lower temperatures of 18, 100, and 156°.

---

[1] This same value (within 0.1) was obtained entirely independently by Prof. Kato and Dr. Sosman, and also by the latter on two separate preparations obtained respectively by recrystallizing the solid salt and by neutralizing ammonium hydroxide and hydrochloric acid.

[2] The exponent for ammonium chloride was assumed to be the same as for potassium chloride at those temperatures where it was not possible to determine it owing to the fact that the measurements did not extend to a higher concentration than 12.5 millinormal.

[3] Vol. 30, p. 339.

TABLE 2.—EQUIVALENT CONDUCTANCE AT ZERO CONCENTRATION.

Substance.	18°.	100°.	156°.	218°.	306°.
NH_4Cl	130.9	415	628	841	1176
$NaC_2H_3O_2$	78.1	285	450	660	924
$NaCl$	109.0	362	555	760	1080
$NaOH$	216.5	594	835	1060	1310
HCl	379	850	1085	1265	1424
NH_4OH	238	647	908	1141	1406
$HC_2H_3O_2$	348	773	980	1165	1268

5. The Equivalent Conductance of Ammonium Hydroxide and Acetic Acid.

In deriving the final values of the equivalent conductance of ammonium hydroxide and acetic acid, all appropriate corrections were applied to the observed data, including that for the conductance of the water and for the small proportion of the ammonia oxidized during the heating. The ammonia used was obtained from two sources—by diluting a specially prepared commercial sample of ammonia water and by distilling liquid ammonia which had stood in contact with sodium. Great care was taken to avoid contamination by the carbon dioxide of the air.

The final values, expressed in the same way as in Table 1, are presented in Table 3. The measurements with acetic acid at 100 and 156° and some of those at 218° were made by Dr. H. C. Cooper, some of those at 218° and all at 306° by R. B. Sosman. Those with ammonium hydroxide at 100 and 156° were made by Yogoro Kato, at 18, 218 and 306° by R. B. Sosman.

TABLE 3.—FINAL VALUES OF THE EQUIVALENT CONDUCTANCE OF AMMONIUM HYDROXIDE AND ACETIC ACID.

Substance.	Concentration.	18°.	100°.	156°.	218°	306°.
NH_4OH	10.0	9.66	23.25	22.31	15.56	...
	30.0	5.66	13.58	12.99	...	...
	80.0	3.47	...	...	5.39	...
	100.0	3.103	7.47	7.17	4.82	1.329
	300.0	1.752	...	...	...	0.785
	500.0	1.325	...	...	...	...
$HC_2H_3O_2$	10.0	14.50	25.10	22.15	14.70	...
	30.0	8.50	14.70	12.95	8.65	...
	80.0	5.23	9.05	8.00	5.39	...
	100.0	4.68	8.10	..	4.82	1.57
	300.0	2.68	...	...	...	0.84

Values were also obtained for ammonium hydroxide at 100 milli-normal at three temperatures between 18 and 100° and at 125°. These values are as follows:

25°.	50°.	75°.	125°.
3.62	5.35	6.70	7.76

Entirely independent determinations made in this laboratory at different times by Messrs. Yogoro Kato, R. B. Sosman, and C. W. Kanolt have given for 100 millinormal ammonium hydroxide at low temperatures closely concordant values, namely, 3.10, 3.10, and 3.11 at 18°, and 3.62 and 3.61 at 25°. Concordant results were also obtained independently by H. C. Cooper and R. B. Sosman for 100 millinormal acetic acid at 18°, namely 4.67 and 4.685.

6. The Ionization of Ammonium Hydroxide and Acetic Acid.

The values of the ratio 100 Λ/Λ_0 corresponding to the percentage ionization (100γ) are given in Table 4. They were obtained by dividing the Λ values given in Table 3 by the appropriate Λ_0 value given in Table 2.

TABLE 4.—PERCENTAGE IONIZATION OF AMMONIUM HYDROXIDE AND ACETIC ACID.

Substance.	Concentration.	18°.	100°.	156°	218°.	306°.
NH_4OH.	10	4.05	3.59	2.46	1 36	..
	30	2.38	2.10	1.43	...	..
	80	1.454	..	...	0.47	..
	100	1.302	1.15	0.79	0.42	0.095
	300	0.735	..	...	...	0.0558
	500	0.556	..	...	..	..
$HC_2H_3O_2$	10	4.17	3.24	2.26	1.26	..
	30	2.45	1.90	1.32	0.743	..
	80	1.504	1.17	0.815	0.463	..
	100	1.346	1.05	...	0.414	0.124
	300	0.771	..	...	...	0.0663

The values for 100 millinormal ammonium hydroxide at the intermediate temperatures are as follows:

25°.	50°.	75°.	125°.
1.338	1.34	1.27	1.02

The values of the ionization constants were calculated from these data by the expression $K = (C\gamma)^2/C(1 - \gamma)$, C being here expressed in equivalents per liter. They are brought together in Table 5. Best values valid for dilute solutions have also been derived, regard being paid to the greater experimental errors in the more dilute solutions and to the deviation from the mass-action law in the more concentrated ones. These are given in italics at the foot of each series.

It is evident from these results that the ionization constant for ammonium hydroxide increases considerably in passing from 0 to 18°, then remains nearly constant up to 50°, and finally decreases with increasing rapidity as higher temperatures are reached, attaining at 306° a value which is only about one two-hundredth of that at 18°. It is also evident that at all temperatures the values for acetic acid are not very different from those for ammonium hydroxide.

TABLE 5.—IONIZATION CONSTANTS × 10⁶ OF AMMONIUM HYDROXIDE AND ACETIC ACID.

Substance.	Equivalents per liter.	18°.	100°.	156°.	218°.	306°.
NH_4OH.........	0.010	17.1	13.4	6.20	1.89	....
	0.030	17.4	13.5	6.24	...	....
	0.100	17.2	13.5	6.28	1.80	0.090
	0.300	16.3	..	..	...	0.094
	0.500	15.6	...	.	...	....
	Best value	*17.2*	*13.5*	*6.28*	*1.80*	*0.093*
$HC_2H_3O_2$	0.010	18.2	10.85	5.23	1.61	....
	0.030	18.5	11.04	5.30	1.67	....
	0.080	...	...	5.36	1.69	....
	0.100	18.3	11.14	..	1.72	0.153
	0.300	18.0	...	..	..	0.132
	Best value	*18.3*	*11.14*	*5.36*	*1.72*	*0.139*
		0°	25°	50°	75°	125°
NH_4OH . .	0.10	13.9[1]	18.0	18.1	16.4	10.4

7. Conductance of Ammonium Acetate Solutions at 18, 100 and 156°.

Experiments by YOGORO KATO.

The hydrolysis experiments were made by measuring the specific conductance of ammonium acetate solutions containing in one case the salt alone and in other cases the salt together with varying quantities of ammonium hydroxide and acetic acid. In the experiments at the temperatures up to 156°, the observed values of the specific conductance were corrected to round temperatures with the help of temperature coefficients derived from the measurements themselves and then further corrected to uniform concentrations by assuming direct proportionality between the concentration and specific conductance through the small concentration interval involved. The so-reduced values are presented in Table 6. In the columns headed "Initial" are given the equivalent conductances obtained from the measurement at the temperature in question before going to the higher temperatures, while in the columns headed "Final" are given the equivalent conductances obtained after returning to the temperature in question from the higher ones. A comparison of these initial and final values in the separate experiments shows the contamination or destruction of the substance that resulted from the heating.

The final data needed for the computation of the hydrolysis, and the calculated values derived from them are presented in Table 7. The column headed L_M contains the most probable values of the specific conductance derivable from the separate values of Table 6, taking into account the contamination and applying a correction for it. In the next column under L_{HA} or L_{BOH} is given the conductance of the acetic

---

[1] This value at 0° is that determined in this laboratory by Kanolt. See *Carnegie Publication*, 63, 290 (1907) or THIS JOURNAL, 29, 1408 (1907).

TABLE 6.—SPECIFIC CONDUCTANCE OF AMMONIUM ACETATE SOLUTIONS AT 18, 100 AND 156°.

Expt. No.	Concentration at 4°.		Specific conductance × 10⁶.				
			18°		100°.		
	$CH_3CO_2NH_4$	CH_3CO_2H.	Initial.	Final.	Initial.	Final.	156°.
1	26.00	.....	2,281	2,276	6,830	...	8,598
2	26.00	...	2,282	2,279	6,821	6,816	8,632
Mean	26.00	....	2,281	2,277	6,825	6,816	8,615
3	10.400	....	946.6	941.9	2,851	2,841	3,583
4	10.400	...	946.9	943.4	2,852	2,839	3,581
Mean	10.400	.....	946.7	942.6	2,851	2,840	3,582
5	26.00	26.47	2,291	2,280	7,157	...	9,885
6	26.00	26.47	2,292	2,286	7,158	7,114	9,925
Mean	26.00	26.47	2,291	2,283	7,157	7,114	9,905
7	26.00	52.00	2,295	2,285	7,166	7,125	10,108
8	26.00	52.00	2,293	2,287	7,164	7,128	10,109
Mean	26.00	52.00	2,294	2,286	7,165	7,126	10,108
9	10.400	21.12	964.0	.....	3,016	...	....
10	10.400	21.13	963.2	958.8	3,015	2,991	4,243
Mean	10.400	21.13	963.6	958.8	3,015	2,991	4,243
11	10.400	52.76	983.2	977.8	3,040	3,011	...
12	10.400	52.76	983.9	974.4	..	...	4,318
Mean	10.400	52.76	983.5	976.1	3,040	3,011	4,318
13	10.400	10.569	957.1	954.3	3,000	2,983	4,166
14	10.400	10.577	957.7	955.0	3,002	..	4,170
Mean	10.400	10.573	957.4	954.6	3,001	2,983	4,168
		NH_4OH.					
15	26.00	51.21	2,298	2,303	7,153	...	10,212
16	26.00	51.21	2,298	2,300	7,168	7,164	10,211
Mean	26.00	51.21	2,298	2,301	7,160	7,164	10,211
17	26.00	25.70	2,290	2,291	7,149	.	10,040
18	26.00	25.70	2,291	2,293	7,145	7,145	9,988
Mean	26.00	25.70	2,290	2,292	7,147	7,145	10,014
19	10.400	10.263	954.7	958.5	2,995	2,991	4,186
20	10.400	10.263	954.7	958.4	2,998	2,992	4,185
Mean	10.400	10.263	954.7	958.4	2,996	2,991	4,185
21	10.400	20.52	960.3	965.5	3,010	...	4,292
22	10.400	20.52	961.4	964.8	3,010	3,013	4,286
Mean	10.400	20.52	960.8	965.1	3,010	3,013	4,289
23	10.400	51.29	979.2	984.2	3,043	...	4,403
24	10.400	51.29	980.9	984.4	3,048	3,050	4,398
25	10.400	50.12	976.1	977.6	....	...	4,388
26	10.400	53.54	981.6	987.7	3,053	...	4,408
27	10.400	*43.93	*966.8	*975.3	*3,036	...	*4,391
Mean	10.400	51.56	979.4	983.5	3,048	3,050	4,399

* Values with an asterisk were not included in deriving the mean.

acid or ammonium hydroxide present. This was obtained by first calculating C_{OH} or C_H from the mass-action equations

$$\frac{C_B C_{OH}}{C_{BOH}} = K_B \text{ or } \frac{C_A C_H}{C_{HA}} = K_A,$$

by substituting for C_B or C_A the ratio $L_{BA}/\Lambda_{0\,BA}$ of the specific conductance of the ammonium acetate (BA) to its equivalent conductance when completely ionized, and then multiplying the value of C_{OH} or C_H

TABLE 7.—SPECIFIC CONDUCTANCE OF THE CONSTITUENTS IN AMMONIUM ACETATE SOLUTIONS.

	Concentration at $t°$.		Specific conductance $\times 10^6$.				
Temperature. $t°$.	Salt. C_{BA}.	Acid (A) or Base (B). C_{HA} or C_{BOH}.	Mixture. L_M.	Acid or base in mixture L_{HA} or L_{BOH}.	Salt in mixture. L_{BA}	Salt alone in water L_S.	Increase. $L_{BA}-L_S$.
18°	25.96	26.43 A	2,291	7	2,284	2,281	3
	25.96	25.66 B	2,290	4	2,286	2,281	5
	25.96	52.76 A	2,294	15	2,279	2,281	—2
	25.96	51.14 B	2,298	9	2,289	2,281	8
				Mean	2,285	2,281	4
	10.387	10.559 A	957	7	950	947	3
	10.387	10.249 B	955	4	951	947	4
	10.387	21.09 A	964	14	950	947	3
	10.387	20.50 B	961	9	952	947	5
	10.387	52.69 A	983	35	948	947	1
	10.387	51.49 B	976	22	954	947	7
				Mean	951	947	4
100°	24.92	25.37 A	7,157	10	7,147	6,825	322
	24.92	24.63 B	7,144	9	7,135	6,825	310
	24.92	50.64 A	7,165	20	7,145	6,825	320
	24.92	49.09 B	7,156	19	7,137	6,825	312
				Mean	7,141	6,825	316
	9.970	10.136 A	3,001	9	2,992	2,851	141
	9.970	9.838 B	2,990	9	2,981	2,851	130
	9.970	20.25 A	3,015	19	2,996	2,851	145
	9.970	19.675 B	3,003	19	2,984	2,851	133
	9.970	50.58 A	3,040	48	2,992	2,851	141
	9.970	49.43 B	3,041	47	2,994	2,851	143
				Mean	2,990	2,851	139
156°	23.68	24.11 A	9,964	5	9,959	8,625	1,334
	23.68	23.40 B	10,004	5	9,999	8,625	1,374
	23.68	48.12 A	10,163	13	10,150	8,625	1,525
	23.68	46.64 B	10,196	14	10,182	8,625	1,557
	9.473	9.631 A	4,193	6	4,187	3,596	591
	9.473	9.348 B	4,169	6	4,163	3,596	567
	9.473	19.243 A	4,278	13	4,265	3,596	669
	9.473	18.694 B	4,270	13	4,257	3,596	661
	9.473	48.06 A	4,360	31	4,329	3,596	733
	9.473	46.97 B	4,381	32	4,349	3,596	753

by $\Lambda_{0\,BOH}$ or $\Lambda_{0\,HA}$. The difference of the values of L_M and L_{HA} or L_{BOH} given in these two columns gives the specific conductance L_{BA} of the salt in the mixture. This is given in the sixth column, and in the seventh column is given the calculated conductance of the salt (L_S) when present in water alone at the same concentration as it has in the mixture. The last column headed $L_{BA} - L_S$ gives the increase of conductance caused by the reduction of the hydrolysis produced by the addition of the base or acid.

8. Hydrolysis of Ammonium Acetate and Ionization of Water at 100 and 156°.

From Table 7 it will be seen that the excess of base or acid causes an increase in the conductance of about 5 per cent. at 100° and 15–21 per cent. at 156°. It will also be seen that at 100° the addition of a quantity of acid or base equivalent to the salt produced as great an increase as a larger quantity, showing that the hydrolysis had been reduced substantially to zero. The effect of the acid was, as it should be, nearly equal to that of the base, the small differences observed being doubtless due to experimental error. The percentage increase was also nearly the same at the two concentrations of the salt (4.6 and 4.9 per cent.) respectively, showing that the hydrolysis does not increase much with the dilution, which is what the mass-action law requires for a salt whose acid and base are both weak. At 156° the second equivalent of acid or base produces a large further increase in conductance, showing that the salt is still somewhat hydrolyzed. Here again the acid and base have not far from the same effect, as they should have on account of the smallness of their ionization constants.

The quantitative calculation of the ionization at 100° is comparatively simple. Since the hydrolysis is reduced to zero by the added acid or base, the increase in specific conductance produced by it when divided by the equivalent conductance Λ_0 (338) of the completely ionized salt gives at once the number of equivalents per cubic centimeter of free acid and base which have been converted into ions. In addition a quantity of the un-ionized salt, corresponding to the increased concentration of its ions, is produced out of the acid and base. To compute this, we have made use of the equation $\frac{(C\gamma)^n}{C(1-\gamma-h)} = K$ (where γ is the fraction ionized and h the fraction hydrolyzed), in which we have determined the constants n and K from the conductances (L_{BA}) of the unhydrolyzed salt (7141 and 2990×10^{-6} at the two concentrations (24.92 and 9.97 milli-equivalents per liter) investigated and from the Λ_0 value for the salt. We have then calculated from the values of L/Λ_0 (which are equal to $C\gamma$) the concentration of un-ionized salt, $C(1-\gamma-h)$, both in the solution containing the salt alone and in that to which acid or base had been added.

The excess of the second value over the first value gives the un-ionized salt, $\Delta C(1-\gamma-h)$, that has been produced out of free acid and base: this added to the quantity ($\Delta C\gamma$) of ions similarly produced gives the quantity of salt in the hydrolyzed state when it is alone present in water; and this divided by the concentration (C) gives the fraction hydrolyzed (h_0). The results of the computations are given in Table 8.

TABLE 8.—HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION CONSTANT OF WATER AT 100°.

C.	100γ or $100 L_S/C\Lambda_0$	$\Delta(C\gamma)$ or $(L_{BA}-L_S)/\Lambda_0$	$\Delta(C(1-\gamma-h))$.	Ch_0.	$100h_0$.	$K_W \times 10^{14}$.
24.92	82.2	0.94	0.21	1.15	4 61	48.5
9.97	85 9	0.411	0 064	0.475	4 76	47.4

It will be seen from Table 8 that the hydrolysis h_0 is only a little greater at 10 than at 25 millinormal. From each of these values the ionization-constant of water ($K_w = C_H \times C_{OH}$) has been calculated, and the results are given in the last column, the concentration being here expressed in equivalents per liter. The calculation was made by means of the mass-action expression $K_w = K_A K_B h^2/\gamma^2$ in which K_A and K_B are the ionization-constants of the acid and base respectively, and h and γ are the hydrolysis and ionization of the salt when present in water alone. This expression is obtained by multiplying together the two ionization equations $K_A = C_H C_A/C_{HA}$ and $K_B = C_B C_{OH}/C_{BOH}$, substituting K_w for $C_H C_{OH}$, γC_S for C_A and C_B, and $C_S h_0$ for C_{HA} and C_{BOH}, and transposing. It will be noted that the two independent values of K_w agree almost completely.

In order to calculate the hydrolysis at 156° from the conductance data it is necessary, since the hydrolysis is not reduced to zero even by the largest quantity of acid or base added, to unite with the empirical relation between the concentrations of ions and un-ionized molecules, the mass-action relation between the concentration of the ions and the products of the hydrolysis. These two expressions, if γ represents the fraction of the salt existing as ions and h the fraction hydrolyzed into free acid and base and C_S and C_{BOH} are the concentrations of the salt and of the added base (or acid) respectively, are

$$\frac{(\gamma C_S)^n}{C_S(1-\gamma-h)} = \text{const.} \qquad (1)$$

and

$$\frac{(\gamma C_S)^2}{(C_{BOH}+C_S h)C_S h} = \frac{\gamma^2}{(C_{BOH}/C_S+h)h} = \frac{K_A K_B}{K_W} = \text{const.} \qquad (2)$$

Or, representing by γ_0 and h_0 the ionization and hydrolysis of the salt when in water alone, and by γ_1 and h_1 these same quantities when the concentration of the salt is the same, but base (or acid) is present in excess at a concentration C_{BOH} and writing r for C_{BOH}/C_S we have:

$$\left(\frac{\gamma_1}{\gamma_0}\right)^n = \frac{1-\gamma_1-h_1}{1-\gamma_0-h_0} \quad (3) \quad \text{and} \quad \left(\frac{\gamma_1}{\gamma_0}\right)^2 = \frac{h_1(r+h_1)}{h_0^2} \quad (4)$$

two simultaneous equations which can be solved for h_0 and h since the other quantities may be derived from the measurements. Thus the ratio γ_1/γ_0 is equal to L_{BA}/L_S (see Table 7), and the separate values of γ_1 and γ_0 are given by the quotients $L_{BA}/C_S\Lambda_0$ and $L_S/C_S\Lambda_0$, Λ_0 being equal to 523. For the exponent n we assumed provisionally the value 1.5, which is that for sodium acetate at this temperature; but after the hydrolysis had been computed for the two different salt concentrations it was obtained by direct application of equation (1) to the mean of the two sets of results, and was thus found to be 1.45; and with this new value of n the calculations were repeated, although this variation in n produced a decrease in h_0 of only 0.7 per cent. of its value both at 23.68 and at 9.473 millinormal. Equations (3) and (4) can be completely solved algebraically for h_1 or h_0, but it is far simpler to use only the incomplete solution obtained by taking the logarithm of equation (3) and eliminating h_0 from it by means of equation (4), whereby results the expression:

$$\log \frac{1-\gamma_1-h_1}{[(1-\gamma_0)\gamma_1/\gamma_0]-\sqrt{h(r+h)}} = (n-1)\log\frac{\gamma_1}{\gamma_0}.$$

This equation can be readily solved for h_1 by trial, and h_0 can then be calculated by (4).

TABLE 9.—HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION CONSTANT OF WATER AT 156°.

C_S.	r.	$100\gamma_0$.	100γ.	$100h$.	$100h_0$.	$K_W \times 10^{14}$.
23.68	1.018 A	70.73	81.66	3.95	17.6	221 A
23.68	0.988 B	70.73	81.99	4.34	18.2	236 B
23.68	2.032 A	70.73	83.23	2.13	17.8	225 A
23.68	1.969 B	70.73	83.49	2.46	18.3	238 B
Mean	......	70.73	...	..	17.97	223 A 237 B
9.473	1.017 A	73.71	85.82	4.40	18.5	224 A
9.473	0.987 B	73.71	85.33	4.16	17.8	208 B
9.473	2.031 A	73.71	87.42	2.30	18.3	219 A
9.473	1.973 B	73.71	87.26	2.33	18.2	217 B
9.473	5.073 A	73.71	88.73	1.00	18.6	226 A
9.473	4.958 B	73.71	89.14	1.06	19.0	236 B
Mean	......	73.71	...	..	18.60	223 A 221 B

The results of the calculations are given in Table 9. The headings will be understood by reference to the preceding paragraph. In computing the ionization constant of water, which was done as before by the expression $K_W = K_A K_B\, h_0^2/\gamma_0^2$, the concentration was expressed in equivalents per liter and the values of K_A and K_B used were 5.67×10^{-6} and $6.28 \times$

10^{-6}, respectively. The letter A after the value of the ratio $r(= C_S/C_B)$ signifies that acetic acid, the letter B, that ammonium hydroxide, was present in excess.

An examination of the values of K_w given in the last column of Table 9 shows that those derived from the experiments where acetic acid was added agree closely with one another not only in case of the successive additions of the acid but also at the two different concentrations of the salt, while those from the experiments where ammonium hydroxide was added are far less concordant whether considered with respect to the successive additions (in the second series) or to the different salt concentrations. This fact, taken in conjunction with the experience that the base solutions are far more liable to contamination, justifies the adoption of the value 223×10^{-14} derived from the experiments with the acid as the best final value for the ionization constant of water at 156°. It is worthy of note, however, that the mean value 229×10^{-14} derived from the experiments with the base is less than 3 per cent. higher than this.

9. Conductance of Ammonium Acetate Solutions at 18, 218 and 306°.

Experiments by R. B. SOSMAN.

The final values for the specific conductance of ammonium acetate solutions at 218 and 306° will next be presented. The observed data were first reduced to round temperatures by means of directly determined coefficients, and were then corrected for the conductance of the impurities

TABLE 10. — SPECIFIC CONDUCTANCE AT ROUND TEMPERATURES OF SOLUTIONS CONTAINING ONLY AMMONIUM ACETATE.

Milli-equivalents per liter.			Specific conductance $\times 10^6$.		
18°.	218°.	306°.	18°.	218°.	306°.
14.57	....	.. .	1311.5	....	....
14.44	....	....	1302	....	....
14.01	11 81	....	1266	3770	....
14.18	12.01	....	1281.5	3830	....
14.30	*11 91*	....	*1290*	*3800*	....
7.10	5.93	....	656.0	1918 5	....
7.11	6.025	....	657.0	1944.5	....
7.045	5.96	....	651.0	1921.5	....
7.085	*5.97*	....	*654.7*	*1928*	....
43.10	....	....	3691	....	....
43.10	....	29.38	3694	....	2412
43.10	....	29.32	....	....	2394
43.10	....	*29.35*	*3693*	....	*2403*
14.335	....	9.97	1294.5	....	812
14.335	....	10.015	1294.5	....	818
14.335	....	*9.995*	*1294.5*	....	*815*

in the water, for that of the water itself, and for that of the added base or acid. The last two corrections, which never exceeded 0.25 per cent., were computed with aid of the ionization constants of the three substances.

Table 10 contains the so-corrected data for the pure salt, and Table 11 those for the salt with an excess of base or acid. In the latter table are given for 218° and 306° in two additional columns (1) the specific conductance (L_0) which the pure salt has at the same concentration as that (C) of the salt in the mixture, and (2) the ratio of the specific conductance (L) of the salt in the mixture to this conductance L_0. The specific conductance L_0 is calculated from that given in Table 10 for nearly the same concentration under the assumption of proportionality between conductance and concentration through the small interval involved.

TABLE 11.—SPECIFIC CONDUCTANCE AT ROUND TEMPERATURES OF AMMONIUM ACETATE SOLUTIONS CONTAINING AMMONIUM HYDROXIDE OR ACETIC ACID.

	Milli-equivalents per liter.		Specific conductance × 10^6.		
Temperature. t.	Salt in mixture. $C \times 10^3$.	Acid (A) or base (B). C_A or $C_B \times 10^3$.	Salt in mixture. $L \times 10^6$.	Salt in water alone. $L_0 \times 10^6$.	Ratio. L/L_0.
218°	11.94	11.88 A	5057	3809	1.328
	12.015	12.075 B	5010	3833	1.307
	11.90	23.61 A	5651	3797	1.488
	11.92	23.41 B	5482	3803	1.442
	11.825	47.38 A	6173	3773	1.636
	11.875	46.75 B	6093	3789	1.608
	6.08	5.985 A	2606	1963	1.328
	6.00	6.25 B	2563	1944	1.318
	6.04	6.25 B	2562		
	6.10	12.055 A	2944	1969	1.495
	6.025	11.78 B	2875	1944	1.476
	6.015	11.78 B	2863		
	5.975	24.12 A	3207	1930	1.662
	6.015	23.62 A	3150	1942	1.622
306°	28.76	31.91 A	3430	2355	1.457
	27.53	88.6 A	4482	2254	1.988
	28.34	68.4 B	4210	2320	1.815
	9.96	10.025 A	1146	813	1.412
	9.965	10.01 A	1150		
	10.01	8.19 B	1092	816	1.338
	9.855	30.06 A	1589	803	1.979
	9.735	25.22 B	1480	794	1.864

10. Hydrolysis of Ammonium Acetate and Ionization of Water at 218 and 306°.

From the data given in Table 11 the hydrolysis of the salt at 218 and 306° was calculated by two different methods.

The first method was that employed by Noyes and Kato and described in Section 8 of this article.

In the second method the ion concentration is, as before, calculated by dividing the specific conductance of the solution (multiplied by 10^3) by the equivalent conductance of the completely ionized salt; and then the concentration of the un-ionized salt is estimated under the assumption that it has the same value as in a solution of an ordinary unhydrolyzed salt of the same ionic type at the same ionic concentration. Then merely by subtracting the un-ionized fraction (u) and the ionized fraction (γ) from unity, the hydrolyzed fraction (h) is obtained; that is, $h = 1 - \gamma - u$. In this calculation the mean value of the ionization of potassium and sodium chlorides was used as a basis. This calculation can give accurate hydrolysis values only when the hydrolyzed fraction is large and the un-ionized fraction very small; but under such conditions, which are in fact realized in the foregoing experiments fairly well at 218° and in much higher degree at 306°, it is the most direct method and a fairly reliable one.

Table 12 contains the results of the calculations. In the fifth and sixth columns are given the values of the percentage hydrolysis ($100\,h$) calculated by the first and second methods, respectively. In the seventh column is given a mean derived from these. Since the results by the second method are more accurate the greater the hydrolysis, in deriving this mean a weight has been assigned to them equal to the percentage hydrolysis, the results by the first method being always given a weight of 100. It is desirable to combine the results by the two methods in some such way as this, since any error in the conductance ratio L/L_0 influences them in opposite directions. In the last three columns of the table are given the values of the percentage hydrolysis ($100\,h_0$) of the salt in pure water at the same concentration C. The values in the first of these columns are derived by the first method simultaneously with those of $100\,h$. Those in the second of these colums are calculated from the mean value of $100\,h$ given in the seventh column by the equation $h_0^2 = \dfrac{h(h + C_B/C)}{(L/L_0)^2}$. Those in the last column are obtained directly by the second method from the conductance in pure water.

A comparison of the values of the percentage hydrolysis ($100\,h$) of the salt in the mixture calculated by the two methods shows at 218° a considerable divergence, especially in the experiments where an excess of base was added. This was doubtless due largely to the destruction of some of the base during the heating. At 306° where this was determined and allowed for, and where the calculation by the second method is more accurate, the agreement is far more satisfactory (except in the first experiment which appears to be affected by some accidental error). From an examination of the values of the percentage hydrolysis ($100\,h_0$) of the salt in pure water it is seen that the experiments in which different

TABLE 12.—HYDROLYSIS AND IONIZATION OF AMMONIUM ACETATE AT 218 AND 306°.

			Salt in mixture.				Salt in pure mixture.			
				Percentage hydrolysis (100h).				Percentage hydrolysis (100 h_0).		
Temperature. t.	Concentration of salt $C \times 10^3$.	Concentration ratio. C_A/C or C_B/C.	Ionization 100γ.	By first method.	By second method.	Weighted mean.	Ionization $100\gamma_0$.	By first method.	From value of h.	By second method
218°	11.91	0	...	..	..	..	43.1	..	..	53.3
	11.94	0.995 A	57.2	35.5	37.4	36.0	43.1	52.1	52.6	..
	11.90	1.984 A	64.1	26.2	29.5	27.0	43.1	51.6	52.4	..
	11.825	4.007 A	70 5	16.5	22.3	17.6	43.1	50.7	51.7	..
	Mean,	....	...	..	..	..	...	51.5	52.2	..
	12.015	1.005 B	56.3	29.6	38.4	32.0	43.1	47 5	49.8	..
	11.92	1.964 B	62.1	21.5	31.8	24.0	43.1	47.4	50.5	..
	11.875	3.937 B	69.2	15.5	23.7	17.1	43 1	49 5	52.1	..
	Mean,	...	...	..	..	..	...	48.1	50.8	..
	5.97	0	...	..	..	..	43.6	..	..	53.7
	6.08	0.984 A	57.8	36.0	38.0	36.5	43.6	52.4	52.9	..
	6.10	1.976 A	65.1	27.1	30.0	27.8	43.6	52.2	52.9	..
	5.975	4.037 A	72.4	17.6	22.0	18.4	43.6	51.8	53.0	..
	Mean,	....	...	..	..	..	...	52.1	52.9	..
	6.02	1.038 B	57.5	30.6	38.4	32.7	43 6	48.6	50.7	..
	6.02	1.957 B	64.3	25.2	30.9	26.5	43.6	50.6	52.0	..
	6.015	3 927 B	70.7	16.1	23.8	17.6	43.6	50.0	52.4	..
	Mean,	....	...	..	..	..	...	49.7	51.7	..
306°	29.35	0	...	..	..	..	8.03	..	..	90.9
	28.76	1.110 A	11.69	93.4	86.3	90.1	8.03	94.8	92.4	..
	27.53	3.218 A	15.96	81.2	81.0	81.1	8.03	91.0	90.9	..
	Mean,	....	...	..	..	..	...	92.9	91.6	..
	28.34	2.414 B	14.56	85.0	82 8	84.0	8.03	91.8	91.1	..
	10.00	0	...	..	..	..	7.99	..	..	91.2
	9.965	1.006 A	11.29	90.2	87.5	88.9	7.99	92.9	91.9	..
	9.855	3.050 A	15.81	86.0	82.3	84.3	7.99	92.7	91.6	..
	Mean,	....	...	..	..	..	...	92.8	91.7	..
	10.01	0.818 B	10.70	86.7	88.2	87.4	7.99	90.3	90.9	..
	9.735	2.591 B	14.91	85.8	83.4	84.7	7.99	92.3	91.5	..
	Mean,	....	...	..	..	..	...	91.3	91.2	..

quantities of acid were added gave very concordant results, whether calculated directly by the first method or from the weighted mean value of the percentage hydrolysis (100 h) for the salt in the mixture. The mean value calculated from the latter is, however, to be considered the most accurate. It will be seen that this agrees well in all cases with the value given in the last column, which was calculated directly by the second method from the conductance of the salt in pure water. To get the best final value from each group of experiments we have combined these two by assigning to the former a weight of 100 and to the latter a weight equal to the percentage hydrolysis. Table 13 contains the final hydrolysis values so obtained, the ionization values for the salt, the ionization-constant of water calculated from them by the equation $K_W = K_A K_B h_0^2/\gamma_0^2$, and the square root of this constant, which represents the concentration C_H of the hydrogen (or hydroxide) ion in pure water.

TABLE 13.—SUMMARY OF VALUES FOR THE IONIZATION AND HYDROLYSIS OF AMMONIUM ACETATE AND FOR THE IONIZATION OF WATER AT 218 AND 306°.

	Ammonium acetate.				
Temperature. $t°$.	Equivalents per liter. C.	Percentage ionization. $100\gamma_0$.	Percentage hydrolysis. $100h_0$.	Ionization-constant of water $\times 10^{14}$. $K_W \times 10^{14}$.	Equivalents of hydrogen-ion per 10^7 liters. $C_H \times 10^7$.
218°	0.012	43.1	52.6	461	21.5
	0.006	43.6	53.2	461	21.5
				Mean, 461	21.5
306°	0.030	8.03	91.3	167	12.9
	0.010	7.99	91.5	170	13.0
				Mean, 168	13.0

11. Summary of the Results on the Hydrolysis of Ammonium Acetate and the Ionization of Water, Ammonium Hydroxide, and Acetic Acid.

The final values of the percentage hydrolysis of ammonium acetate in 0.01 normal solution, of the ionization constants of ammonium hydroxide, acetic acid, and of water ($K_W = C_H C_{OH}$), and of the equivalents (C_H) of hydrogen ion or hydroxide ion present in one liter of pure water, obtained as described in this article, are summarized in Table 14. We have also included in the table values of the ionization constant of water at 0, 18, and 25° derived by Dr. C. W. Kanolt[1] from experiments made by him in this laboratory upon the conductance of ammonium hydroxide and of diketo-tetrahydrothiazole and upon the hydrolysis of the salt of this base and acid, in order to enable the results at the higher temperatures to be compared and combined with these at lower temperatures. The value given in the table for the hydrolysis of ammonium acetate at 18° is not based on direct measurements, but has been computed from the ionization constants of water, ammonium hydroxide, and acetic acid at that temperature.

---

[1] THIS JOURNAL, 29, 1414 (1907).

TABLE 14.—HYDROLYSIS OF AMMONIUM ACETATE AND IONIZATION OF WATER, AMMONIUM HYDROXIDE AND ACETIC ACID.

Temperature. $t°$.	Hydrolysis of ammonium acetate. $100h$.	Ionization constant of water. $K_W \times 10^{14}$.	Hydrogen-ion concentration in pure water. $C_H \times 10^7$.	Ionization constant of ammonium hydroxide. $K_B \times 10^6$.	Ionization constant of acetic acid. $K_A \times 10^6$.
0	.....	0.089	0.30	13.9	....
18	(0.35)	0.46	0.68	17.2	18.3
25	.....	0.82	0.91	18.0	....
100	4.8	48	6.9	13.5	11.14
156	18.6	223	14.9	6.28	5.36
218	52.7	461	21.5	1.80	1.72
306	91 5	168	13.0	0.093	0.139

It will be seen that the hydrogen-ion concentration in pure water increases with extraordinary rapidity between 0 and 100°; namely, by about 3-fold between 0° and 25° and 7½-fold between 25 and 100°. Between the latter temperature and 218° the ionization increases more slowly, afterwards passes through a maximum (which appears to lie between 250 and 275°), and finally decreases. When it is considered that the ionization of weak acids and bases, as shown by the data for ammonium hydroxide, acetic acid, and phosphoric acid, decreases rapidly with rising temperature, and that this acts in the same direction in increasing the hydrolysis of salts as does an increase in the ionization of water, it will be evident that the tendency of salts to hydrolyze is enormously greater at high temperatures, as is well illustrated by the values given for ammonium acetate.

The great increase in hydrolysis is also exemplified by the hydrolysis values for sodium acetate and ammonium chloride in 0.01 normal solution that can be calculated from the preceding data: these salts, which at 18° are 0.02 per cent. hydrolyzed, are found to be 1.6 per cent. at 218° and 3.4 to 4.1 per cent. hydrolyzed at 306°.

The fact also deserves mention that the values of the concentration of the hydrogen ion in water at 0, 18, and 25° as derived from Kanolt's hydrolysis experiments are 16 to 20 per cent. lower than those obtained by Kohlrausch and Heydweiller[1] from the conductance of their purest water, and by Lunden[2] from his hydrolysis experiments.

From these ionization constants (K_w) approximate values of the internal-energy increase ΔE attending the reaction $H_2O = H^+ + OH^-$ (the so-called heat of ionization) can be computed by the familiar equation[3] derived from the Second Law of Energetics: $d \log K_w/dT$

---

[1] *Ann. Phys.*, [3] 53, 209 (1894); [4] 28, 511 (1909).

[2] Publications of Nobel Inst., 1, No. 8, p. 16 (1907).

[3] This equation ceases to be even approximately exact at high temperatures where the vapor pressure of water becomes very large. The exact expression, which may be derived through the consideration of an appropriate cyclical process, is as follows:

$\Delta E/RT^2$. This is best done by integrating it under the assumption that ΔE is a linear function of the temperature as expressed by the equation $\Delta E = \Delta E_0 + \alpha RT$. The integral then has the form

$$\log \frac{K_2}{K_1} - \alpha \log \frac{T_2}{T_1} = \frac{\Delta E_0}{R} \frac{T_2 - T_1}{T_1 T_2}.$$

From the values of the ionization constant K at 0°, 25°, and 100°, the values of the constants ΔE_0 and α have been found to be 28460 and —24.923, respectively. Therefore, the general equation for the energy increase attending the ionization becomes

$$\Delta E = 28460 - 49.5\,T,$$

and that for the ionization constant becomes

$$\log_{10}(10^{16}K) = 84.450 - \frac{6222}{T} - 24.923 \log_{10} T.$$

The values of the energy increase in calories and of the ionization constant of water as calculated by these expressions are given in Table 15.

TABLE 15.—INTERNAL-ENERGY INCREASE ATTENDING THE IONIZATION OF WATER AND ITS IONIZATION CONSTANT CALCULATED BY AN EMPIRICAL EQUATION.

Temperature.	Energy increase. ΔE.	Ionization constant $K \times 10^{14}$.
0	14950	0.088
18	14055	0.46
25	13710	0.81
50	12470	4.5
75	11230	16.9
100	9995	48
128	8610	114
156	7225	217
218	(4155)	(512)

These values of the ionization constant at 0, 25, and 100° necessarily agree with the directly determined ones given in Table 14. It is of interest to note, however, that this is also true of the calculated value at 156°, which shows that up to this temperature the assumed equations hold

$$\Delta E = RT^2 \frac{d \log Kw}{dT} + \Delta V . T^2 \left[\frac{d(p/T)}{dT} - \frac{d(P/T)}{dT} \right]$$

where ΔE is the energy increase and ΔV is the volume increase that attends the ionization of one mol. of water under the pressure $p - P$, which is substantially identical with the vapor pressure p, since the osmotic pressure P is in this case negligible in comparison. Approximate values of ΔV up to 140° have been computed by Tammann (*Z. physik. Chem.*, **16**, 144 (1894)) which show it to be equal to about —26 cm. at 140°; and since it is shown to be increasing at a rate roughly proportional to the compressibility of water, it probably has a value in the neighborhood of —40 cm. at 218°. Assuming this to be the case, the last term in the above equation can, with the help of the existing vapor-pressure data, be shown to have a value of about —170 calories at 218°, while the value of ΔE as computed by the linear equation is 4155 at 218°. Thus at temperatures above 200° this last term begins to form a substantial part of the whole.

true, and that therefore the values interpolated for the intermediate temperatures between 0 and 156° are doubtless substantially correct. Even at 218° the difference between the observed and calculated values (461 and 512), though doubtless real, is not very large; it lies in such a direction as to indicate that the energy change ΔE is decreasing at a more rapid rate at temperatures above 156° than at the temperatures below it. This is also shown by the fact that the ionization constant at 306° is much less than at 218°, while according to the linear equation the value of ΔE should become zero, and therefore that of the ionization constant K should become a maximum, very near the former temperature, namely, at 302°. The real maximum value of the constant seems to lie between 250 and 275°. Above this temperature ΔE assumes a negative value; and therefore the neutralization of completely ionized acids and bases would be attended by an absorption of heat.

It may also be mentioned that at the lower temperatures the calculated values agree well with the heat of neutralization directly measured by Wörmann,[1] who found for hydrochloric and nitric acids when neutralized with potassium and sodium hydroxides as mean values 14,710 calories at 0° and 13,410 calories at 25°.

It seems worth while to call attention to a possible theoretical explanation of the fact that water, unlike all other substances thus far investigated, continues to increase in ionization up to so high a temperature as 250 or 275°. This phenomenon may well arise from the facts that water at low temperatures is a highly associated liquid containing only a small proportion of H_2O molecules, and that this proportion increases rapidly with rising temperature. Therefore, even through the fraction of H_2O molecules dissociated into H^+ and OH^- ions may decrease steadily, yet the actual concentration of these ions continues to increase until a large proportion of the complex water molecules have been depolymerized.

To the Carnegie Institution of Washington we desire to express our great indebtedness for the financial assistance by which the execution of this investigation has been made possible.

BOSTON, November, 1909.

THE REACTION BETWEEN AMMONIUM CHLORIDE AND POTASSIUM DICHROMATE WHEN HEATED.

BY G. B. FRANKFORTER, V. H. ROEHRICH AND E. V. MANUEL.

Received December 8, 1909.

Doubtless every one who has given a course of lectures in general chemistry has used the potassium dichromate and ammonium chloride method for the preparation of nitrogen, inasmuch as this is one of the methods mentioned in nearly all of the old as well as in some of the new texts of inorganic chemistry. One of us using this method some years ago had reasons to question the correctness of the reaction as ordinarily given:

---

[1] *Ann. Physik.*, [4] 18, 793 (1905).

$$2NH_4Cl + K_2Cr_2O_7 = Cr_2O_3 + 2KCl + 4H_2O + N_2.$$

The matter was not carefully examined until some time later when the subject was taken up and carefully investigated. It required but a few experiments to show that the gas liberated by heating a mixture of ammonium chloride and potassium dichromate is not pure nitrogen. On the contrary, it contains, in addition to nitrogen, such amounts of nitric oxide and nitrogen peroxide as would make the simple equation given above entirely out of the question. In fact, the gas obtained is so rich in nitric oxide that when exposed to the air the brown peroxide color becomes very distinct. It was found, on looking up the literature, that Ramon de Luna,[1] in a letter to Dumas, first described the method and is responsible for the above equation. He intimated, however, that the nitrogen obtained was not pure unless passed through a solution of iron sulphate. It is evident from this last statement that he was aware of the presence of the oxides of nitrogen, although no mention of their presence was made and no attempts made to determine the quantity of gas liberated. From a number of analyses made under widely varying conditions, the writers have concluded that the above reaction is only correct in so far as water, some potassium chloride and some nitrogen are formed in the reaction. Chromic oxide is formed only after prolonged heating at a comparatively high temperature. Nitric oxide and nitrogen peroxide are probably formed when the mixture is heated at any temperature above 210°.

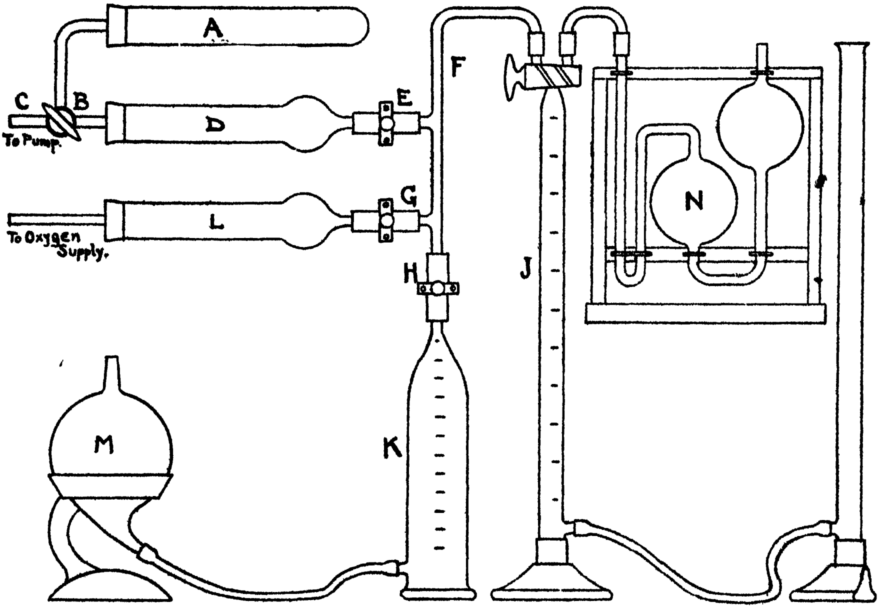
The gas first examined was prepared by using the quantities of salts recommended by de Luna, namely, equal parts of ammonium chloride and potassium dichromate and heating in a hard glass tube containing a delivery tube for collecting the gas over water. In these first experiments we were unable to detect nitrogen peroxide in the gas liberated, doubtless on account of its solubility in water. Later when the gases were collected over mercury, nitrogen peroxide was always found, varying, however, from a very small quantity to 3.5 per cent. Nitric oxide varied from 3 to 50 per cent. of the total gas liberated.

In our first experiments, great difficulty was experienced in preparing the gas for analysis, as it was necessary to remove every trace of air from the apparatus before the analysis was begun. After many experiments with different forms of apparatus, the following figure was constructed and used in most of the subsequent analyses: The hard glass tube A is connected with drying tube D by means of the three-way cock B; tube C is connected with an air pump. D is connected with F by means of a heavy rubber connector and pinchcock, E. F is connected with gas burette J, gas holder K, and drying tube L, for furnishing pure oxygen. The leveling tube M is connected with holder K by means of a heavy rubber tube. J is connected with gas pipette N by means of a three-way cock.

---

[1] *Ann. chim. phys.*, [3] 68, 183.

To prepare the gas for analysis, the hard glass tube A was filled with the mixture of ammonium chloride and potassium dichromate and connected with B. Gas burette J and reservoir K were filled with mercury up to the capillary tube F. Stopcock B was turned so that A and D were in connection with the air pump. The air was then exhausted and the apparatus washed out twice with pure nitrogen prepared from ammonium nitrite. Finally a vacuum of less than one millimeter was obtained and the experiment begun by gradually heating A. The gases first liberated were collected in the reservoir K until a sufficient quantity was obtained for examination, analysis being made of the gas liberated at different temperatures, beginning at 210°.



Analysis of the Gas.—As both nitric oxide and nitrogen peroxide were present, a method for the determination of these gases was used, depending upon the fact that nitrogen peroxide is soluble in potassium hydroxide, while nitric oxide is not. All the determinations in the first table of analyses were made over mercury with Hempel's apparatus for the exact analysis of gases over mercury. The nitrogen peroxide was first removed by means of caustic potash. The nitric oxide was then determined by adding to the residue a known volume of pure oxygen, and noting the change in the combined volumes as indicated by the following equation:

$$2NO + O_2 = 2NO_2.$$

Finally the results were checked by absorption of the nitrogen peroxide formed by means of potassium hydroxide.

In collecting the gas, preparatory to analysis and during the process of analysis, difficulties arose on account of the nitrogen peroxide attacking the mercury. We were unable to completely prevent this although by carefully drying the gases before coming in contact with the mercury, the action was greatly reduced. The following table gives the percentage by volume of the total amount of gas liberated on heating equal parts of the salts to a dull red heat:

TABLE I.

	N.	NO.	NO_2.
1.	55.3	41.1	3.1
2............	55.6	42.2	2.2
3	54.6	44.0	1.4
4..	50.1	48 5	1.4
5	54.3	44.6	1.1
6	48.7	50.1	1.2
Average......	53.1	45.1	1 7

An average of twenty analyses gave numbers differing but slightly from the above average. The first two analyses were made without completely evacuating the apparatus before heating. This doubtless accounts for the increased amount of nitrogen peroxide. It is not possible that the peroxide found in the other analyses can be due to air as the apparatus was thoroughly evacuated before heating.

In the above analyses, no attempt was made to regulate the temperature. These first experiments were made by heating the mixture with a bunsen lamp until no more gas was given. The analysis was then made of a sample of the total amount of gas liberated. Although the reaction apparently began at a low temperature, it required a dull red heat to complete it and to change the dichromate over into chromic oxide.

That exact data might be obtained concerning the changes which take place at different temperatures, an electric heater with a thermostat was constructed. The apparatus consisted of a resistance coil packed in asbestos. This coil enclosed a double-walled mercury jacket which in turn surrounded the bulb containing the mixture of chloride and dichromate. The mercury in this jacket transmitted the heat to the bulb and at the same time, by expansion and contraction, opened and closed a shunt for regulating the temperature. The bulb was made with a neck for introducing a thermometer and a delivery tube for the gases. With this apparatus the whole bulb containing the mixture could be uniformly heated and the temperature could be easily kept within a range of two degrees. The gases were determined gravimetrically. The water formed in the reaction was collected in a phosphoric anhydride bulb and the nitrogen peroxide was taken out by a small potash bulb. In the first experiment the nitric oxide was removed by passing the gas through a piece of apparatus consisting of a sodium peroxide tube followed by a pyrogallate bulb, the latter being used for the purpose of retaining any oxygen which might be liberated by traces of moisture coming in contact with the peroxide. Later this gas was determined by absorption in a ferrous sulphate solution. The nitrogen was collected and measured over water.

The following table of weights was obtained by heating a mixture of two molecules of ammonium chloride and one molecule of potassium dichromate at a temperature of 288–290° until gas ceased to come off. This required about eight hours. Previous to heating, the whole apparatus was carefully swept out with pure nitrogen. The absorption bulbs were removed at the end of the experiment and weighed. That these data may be compared with those of Table 1, the nitrogen and the oxides of nitrogen have been converted into percentages by volume. The following is a result of three analyses:

TABLE 2.

Analysis.	I. Grams.	II Grams.	III. Grams.
Weight of mixture	7.5000	12 046	12.046
H_2O	0.6470	1.446	1.3280
NO_2	0.0127	0.0272	0.0052
NO	0.0072	lost	0.0269
N_2	0.3280	0.6000	0.4663
$Cr_2O_3.2H_2O$	.	4.520	.....
NO_2 by volume	2.26	.....	0.63
NO by volume	1.97	.....	5.08
N_2	95.77	.....	94.29

In these determinations the ammonium chloride and potassium dichromate were not all decomposed, both being found unchanged in the residue after heating at 290°. In fact, the water and nitrogen liberated were only about one-half of the amount which should have been given off, had the reaction been complete and all of ammonium chloride and dichromate decomposed.

A comparison of this table with Table 1 will show that entirely different reactions take place when the mixture is heated at 290° and at a dull red heat. This is not only evident from the composition of the gas liberated but also from the nature of the residue left after lixiviation.

Hydrated Chromic Oxide, $Cr_2O_3.2H_2O$.—No change takes place in a mixture of ammonium chloride and potassium dichromate until a temperature of 210° is reached. At this point slow decomposition begins and the mixture turns yellowish brown, due to the formation of chromium dioxide.[1] If the temperature is raised to 260° a slate-colored residue remains which, on lixiviating with water, leaves small greenish black iridescent spangles. This substance proved to be a hydrated oxide of chromium containing, however, a trace of chlorine which was very difficult to remove. Two analyses of this substance gave the following:

I. 0.5090 g. substance gave 0.0978 g. H_2O = 19.2 per cent.

II. 2.9608 g. substance gave 0.6474 g. H_2O = 21.6 per cent.

$Cr_2O_3.2H_2O$, $2H_2O = 19.15$.

The samples used in the above analyses were prepared at different times and under different conditions. The oxide used in the first analysis was dried in a vacuum desiccator, while that used in the second was dried in an air bath at 100°.

The change which takes place when a mixture of ammonium chloride and potassium dichromate is heated may be further shown from the fact that not only a change of temperature but also a change in the proportions of the salts will change the reaction. For instance, when a mixture of one part of ammonium chloride and four of the dichromate is heated to 370° a gray residue remains containing a trace of a violet substance, presumably the trichloride, as chromium chloride was found in the residue. When the above proportions were used no unchanged dichromate was found in the residue after heating. However, a strong odor of ammonia was noticed when the retort was opened.

When the proportions were reversed, using one part of ammonium chloride and four of the dichromate and the mixture heated to 370°, a black residue together with some unchanged dichromate remained. No violet compound was found.

The first change which evidently takes place on heating a mixture of ammonium chloride and potassium dichromate is the dissociation of the ammonium chloride. By diffusion, the ammonia passes up through the mixture and into the drying bulbs more rapidly than does the hydrochloric acid. There is left, then, in the mixture, free hydrochloric acid which reacts with the dichromate. By varying the temperature and the amount of hydrochloric acid, a series of reactions may take place giving all of the substances which have been found. The following may represent some of these equations:

1. $2NH_4Cl + 2HCl + 2K_2Cr_2O_7 = 4KCl + 2Cr_2O_3 + NO + NO_2 + 5H_2O$.

2. $3NH_4Cl + 2HCl + 2K_2Cr_2O_7 = 4KCl + 2Cr_2O_3 + N_2 + NO + Cl + 7H_2O$.

3. $2NH_4Cl + 4HCl + 2K_2Cr_2O_7 = 4KCl + 2Cr_2O_3 + 2NO + Cl + 6H_2O$.

---

[1] *Bull. soc. chim.*, 40, 168; *Proc. Chem. Soc.*, 24, 27.

4. $4NH_4Cl + 6HCl + 2K_2Cr_2O_7 = 4KCl + Cr_2O_3 + 2CrCl_3 + 2N + 11H_2O$.

5. $2NH_4Cl + 8HCl + 2K_2Cr_2O_7 = 4KCl + 2Cr_2O_3 + N_2 + 3Cl_2 + 8H_2O$.

At a high temperature and especially where an excess of the dichromate is used, chlorine is liberated as indicated in equations 2 and 3.

Some of the above equations are only possible, of course, when a part of the dissociated ammonia has been eliminated from the reaction as for instance by the phosphoric anhydride bulb. Any free ammonia left would react with the oxides of nitrogen and chlorine, liberating free nitrogen.

The substances above mentioned are by no means the only ones formed when the above mixtures are heated. There is formed in addition to the above substances, a small amount (representing about one per cent.) of a substance which, when brought in contact with water, liberates pure nitrogen. This substance appears to be a chromyl nitride, and is now under further investigation.

A summary of the principal facts noted above may be stated as follows:

1. The reaction between ammonium chloride and potassium dichromate when heated is not correct as ordinarily given.
2. The oxides of nitrogen are always present in the gas liberated.
3. Both ammonia and chlorine are liberated under certain conditions.
4. Other chromium compounds besides the common oxide are formed.
5. A nitride, presumably trichromyl nitride is formed.
6. The complex nature of this reaction is due in very large measure to the dissociation of ammonium chloride.

UNIVERSITY OF MINNESOTA, MINNEAPOLIS.

THE ACTION OF THIONYL AND SULPHURYL CHLORIDES ON MERCURY AND MERCURIC OXIDE.

BY H. B. NORTH.

Received December 7, 1909.

The action of sulphuryl chloride on mercuric oxide has already been studied by Spelta.[1] He states that red oxide of mercury and sulphuryl chloride do not react in the cold or even after prolonged heating in sealed glass tubes.

Yellow oxide of mercury, on the contrary, was found by Spelta to react with sulphuryl chloride when the two are heated together in sealed glass tubes at 150°. He indicates that the reaction proceeds according to the equation

$$(a) \quad 2HgO + SO_2Cl_2 = HgCl_2 + HgSO_4$$

or

$$(b) \quad HgO + SO_2Cl_2 = HgCl_2 + SO_3$$

---

[1] *Gazz. chim. ital.*, 34, 262 (1904).

depending upon the relative quantities of oxide and reagent employed.

During the course of a general research on the action of thionyl and sulphuryl chlorides on metals and metallic oxides, the author has had occasion to repeat the work of Spelta. The results, however, do not entirely concord with those obtained by the latter, as no great difficulty was experienced in causing sulphuryl chloride and red mercuric oxide to react.

Sulphuryl Chloride and Mercuric Oxide.—When *yellow* mercuric oxide and sulphuryl chloride were brought together at the ordinary temperature and pressure, reaction commenced immediately, but proceeded very slowly. After standing several days the yellow color had entirely disappeared. The white powder which remained consisted of a mixture of mercurous and mercuric chlorides.

Small quantities of the yellow oxide with an excess of sulphuryl chloride were then heated together in sealed glass tubes at a temperature of about 150°. Reaction was complete after a few hours. The solid contents of the tubes appeared in the form of clear, colorless crystals, some of which were over 1 cm. in length. When the tubes were opened, considerable pressure was noted and dense white fumes, consisting in part of sulphur trioxide, were given off.

The crystals were dried between filter papers and analyzed. Qualitative tests failed to show more than mere traces of sulphate, and this was probably due to sulphur trioxide formed in the reaction. Quantitative analysis showed the crystals to be mercuric chloride. From this it is evident that, as reported by Spelta, the reaction proceeds according to the equation "*b*" heretofore given. That no mercuric sulphate was present was of course due to the fact that a considerable excess of sulphuryl chloride was employed.

Red oxide of mercury, in contrast to the yellow compound, did not immediately react with sulphuryl chloride in the cold, but after standing several days, some reaction had taken place for the mixture was found to contain traces of both mercurous and mercuric chlorides. As previously stated, no great difficulty was encountered in causing them to react by heating in sealed glass tubes. Moreover, the temperature necessary was only 160–180°. Reaction was complete after 15 or 20 hours.

The results were the same as those obtained from the experiment with the yellow oxide. The crystals were large and clear, and when the tubes were opened dense white fumes containing sulphur trioxide were evolved. Likewise the crystals analyzed to mercuric chloride and showed a mere trace of sulphate.

Why this result differs from that obtained by Spelta is difficult to explain. It is possible, however, that the oxide used by him had been prepared at a higher temperature, in which case it would naturally show greater resistance to the action of the reagent.

Sulphuryl Chloride and Mercury.—Sulphuryl chloride was found to have no action upon metallic mercury under ordinary conditions of temperature and pressure. But when heated together in sealed glass tubes at 160–180°, reaction was complete after a few hours and a well crystallized product resulted. Great pressure was developed and much sulphur dioxide was evolved when the tubes were opened. The crystals analyzed to mercuric chloride and contained no sulphate. It is probable that the reaction is a simple one, as expressed by the following equation:

$$Hg + SO_2Cl_2 = HgCl_2 + SO_2.$$

When an excess of mercury was used, the solid product formed was noncrystalline, and consisted entirely of mercurous chloride.

Thionyl Chloride and Mercuric Oxide.—A very strong reaction resulted upon bringing thionyl chloride into contact with *yellow* mercuric oxide. Much heat was evolved and the solid contents of the tube became white. Reaction stopped after a few minutes The white mass was found to be a mixture of the two chlorides of mercury. When *red* oxide of mercury was employed, the same reaction took place, but much more slowly.

In order to obtain better products, both reactions were carried out in sealed glass tubes at about 160°. After heating several hours the tubes presented the same appearance. The crystals were large, and the supernatant liquid was clear but slightly yellowish in color.

Upon opening the tubes they were found to be under no pressure and no sulphur dioxide was evolved. The crystals were mercuric chloride and contained no sulphate. The author is of the opinion that reaction takes place with the formation of sulphuryl chloride and sulphur monochloride according to the following equation:

$$HgO + 5SOCl_2 = HgCl_2 + 3SO_2Cl_2 + S_2Cl_2.$$

The fact that no gaseous products were formed seems to substantiate this view. Furthermore, the supernatant liquid, after decomposition by water, gave a strong test for sulphuric acid. When thionyl chloride is decomposed by water the products are hydrochloric acid and sulphur dioxide.

If the above reaction is true, it can take place only when a large excess of thionyl chloride is present. To ascertain the truth of this, other tubes were prepared, care being taken to employ less of the reagent. In these tubes considerable pressure was developed due to sulphur dioxide formed. The reaction probably proceeds according to the equation

$$HgO + SOCl_2 = HgCl_2 + SO_2.$$

Thionyl Chloride and Mercury.—Thionyl chloride, like sulphuryl chloride, was found to have no reaction upon metallic mercury in the cold. But after heating in sealed glass tubes for a few hours at 150°, reaction was complete. As in the case of thionyl chloride and mercuric oxide, when a large excess of reagent was employed, no sulphur dioxide was formed and the tubes were therefore under no pressure. But when only a slight excess was employed, considerable pressure was developed. In both cases a strong odor of sulphur monochloride was noticeable while the crystals were being dried, and the filter paper was colored slightly yellow, evidently by this compound. Reaction probably proceeds according to one of the two following equations, depending upon the amount of thionyl chloride used:

$$Hg + 4SOCl_2 = HgCl_2 + 2SO_2Cl_2 + S_2Cl_2$$
$$3Hg + 4SOCl_2 = 3HgCl_2 + 2SO_2 + S_2Cl_2.$$

When an excess of mercury was employed, mercurous chloride, sulphur dioxide and sulphur monochloride were the products.

The author has heretofore investigated many reactions between thionyl chloride and metals or oxides, but the two above-mentioned reactions, in which a large excess of thionyl chloride was used, are the first he has found in which no pressure is developed or in which sulphur dioxide is not one of the final products. It has not been possible to positively identify sulphuryl chloride inasmuch as the amount of thionyl chloride used was small, and the boiling points of the two liquids are too close to allow of definite tests by fractional distillation of small quantities. However, considering the facts heretofore given, the author has little doubt that the reaction proceeds with the formation of sulphuryl chloride, according to the equations given.

The two reactions with sulphuryl chloride are also noteworthy inasmuch as they are the first reactions found for this reagent in which sulphur trioxide or a sulphate is produced.

Faculté des Sciences de Paris,
Laboratoire de chimie générale.

[Contribution from the Laboratories of General and Physical Chemistry of the University of Chicago.]

DOES CALOMEL FURNISH ANOTHER CONTRADICTION OF THE THEORY OF HETEROGENEOUS DISSOCIATION EQUILIBRIUM?

By Alexander Smith.

Received January 4, 1910.

As is well known, undried ammonium chloride gives, at 360°, values for the vapor density corresponding to the formula ½ NH_4Cl, and indicating complete dissociation. Brereton Baker,[1] however, using the Victor Meyer and the Dumas methods found that the salt, when elaborately dried, gave at the same temperature values corresponding very nearly to the formula NH_4Cl. Since, in each case, to operate the method, about one atmosphere pressure of the vapor was necessary, it is fair to infer that in the first case the undried solid was in equilibrium with a minute partial pressure of the undissociated molecules, while in the second case the dried solid was in equilibrium with something like 760 mm. pressure of the same molecules. Abegg[1] has recently called attention to this anomaly, consisting in an apparent contradiction of the theory of heterogeneous dissociation equilibrium. At his instance, F. M. G. Johnson[2] has measured the vapor pressures of the salt, and established the fact that at about 340° the dried and undried forms of the substance do give undissociated and dissociated vapor, respectively, and yet exhibit equal pressures (amounting to 760 mm.) of the saturated vapors. The existence of the anomaly is therefore demonstrated.

---

[1] *J. Chem. Soc.*, 65, 615; 73, 475.

Now Brereton Baker[3] found likewise that dried calomel, at 445°, gave vapor densities corresponding very nearly to the formula Hg_2Cl_2 (average density, 435; theory for Hg_2Cl_2, 470). Yet, as is well known, calomel when undried gives at this temperature vapor densities corresponding to the formula HgCl (or $Hg + HgCl_2$). The purpose of this paper is to point out that calomel appears therefore to exhibit the same anomaly as does ammonium chloride. The inference is, in the case of calomel, to a very slight degree less certain of confirmation, since at 445° calomel gives a vapor pressure of about two atmospheres, and at 760 mm. the vapor is therefore only half saturated and is not in equilibrium with the solid. It seems, nevertheless, probable that, at one and the same temperature, dried calomel will be found to be in equilibrium with 760 mm. pressure of Hg_2Cl_2 molecules, although undried calomel will give the same total pressure, and only a minute partial pressure of the undissociated molecules. Experiments to ascertain whether calomel does actually exhibit this anomaly are now being made in this laboratory.

The matter is of great significance for the explanation of Abegg's anomaly. Among the suggested explanations, the two most plausible are: (1) Abegg's[4] that the heat of formation of gaseous, undissociated NH_4Cl happens to be equal to the heat of dissociation of gaseous NH_4Cl into $NH_3 + HCl$; and (2) Wegscheider's[5] that it is a case of polymorphy, and suspended transformation in the dry sample, accompanied by accidental identity of the high vapor pressure of NH_4Cl molecules from the form unstable at 360° with the vapor pressure of NH_3 and HCl molecules from the form stable at 360°. Either explanation depends on a coincidence which could not occur in precisely the same way with a different substance unless the coincidence was due to some as yet unrecognized general relation, and not to accident.

---

[1] *Z. physik. Chem.*, 61, 455.

[2] *Ibid.*, 61, 457.

[3] *J. Chem. Soc.*, 77, 646.

[4] *Z. physik. Chem.*, 62, 608.

[5] *Ibid.*, 65, 97.

CHICAGO, December 20, 1909.

THE CONDENSATION PRODUCTS OF MELLITIC ACID WITH META-AMINO PHENOL AND THEIR BEARING ON THE RELATIONSHIP OF COLOR AND FLUORESCENCE TO CONSTITUTION.

BY OSWALD SILBERRAD AND CHARLES SMART ROY.

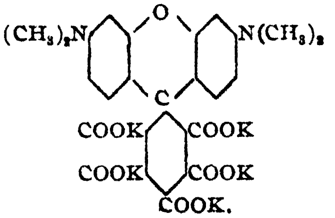
Received November 27, 1909.

In a previous paper by one of the authors on the condensation products of mellitic[1] and pyromellitic acids with resorcinol,[2] much evidence was brought to show that color and fluorescence are not necessarily dependent on quinoidal structure.

The present work deals with the corresponding rhodamines, and fully confirms the conclusions arrived at in the previous paper. Coupled with, and to some extent interdependent on these results is the possibility of ascribing fluorescence to oscillatory tautomerism. As will be shown below it is illogical and impractical to formulate all the compounds dealt with in this paper on the quinone system, and since they are without exception intensely colored and strongly fluorescent, it becomes evident that a quinoidal grouping is not a necessarily integral part of a colored and fluorescent compound.

The compounds dealt with in this paper may be divided into three groups, namely:

1. *Monoxanthyl Derivatives*, of which tetramethyldiaminoxanthylbenzenepentacarboxylic acid may be taken as typical—formula I represents the potassium salt,



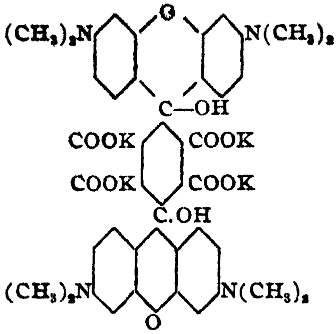
I.

2. *Dixanthyl Derivatives.*—These exist in two modifications according to whether the xanthyl groups are para or meta to one another. They behave as tetrabasic acids:

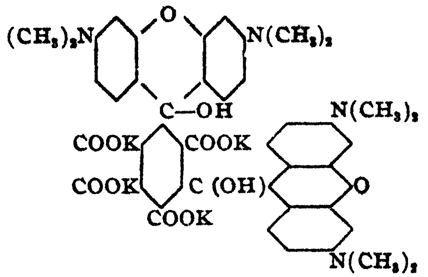
---

[1] The mellitic acid required for this investigation was manufactured from charcoal according to British Patent No. 24,662, '07.

[2] Silberrad, *J. Chem. Soc.*, 89, 1789 (1906).



II.



III.

The potassium salt of

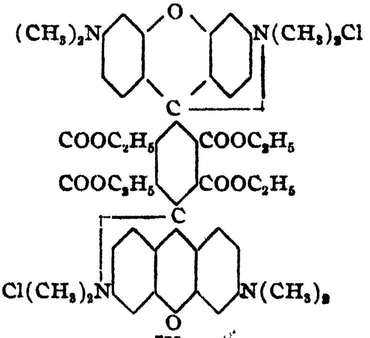
II. Octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylic acid

and of

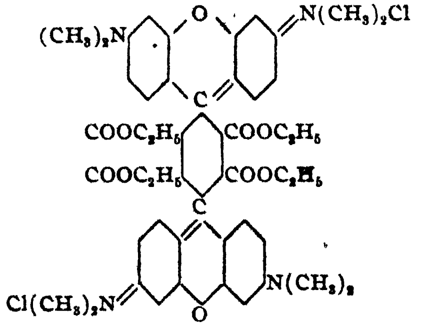
III. Octamethyltetraminodihydroxymetadixanthylbenzenetetracarboxylic acid.

3. *Trixanthyl Derivatives*, of which hydrated dodecamethylhexaminotrihydroxysymtrixanthylbenzenetricarboxylactone may be regarded as typical (formula VI). This is a well-defined base which gives rise to a readily soluble hydrochloride.

All these compounds form anisolines which may with equal readiness be formulated either as carbinol (IV) or quinone derivatives (V).



IV.



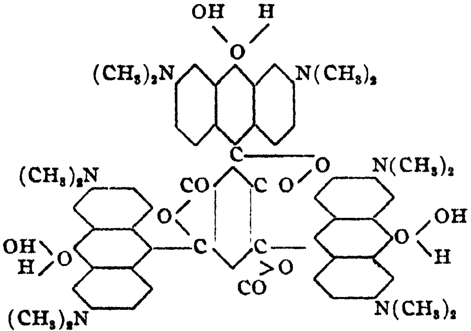
V.

Octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylic ethyl ester dichloride.

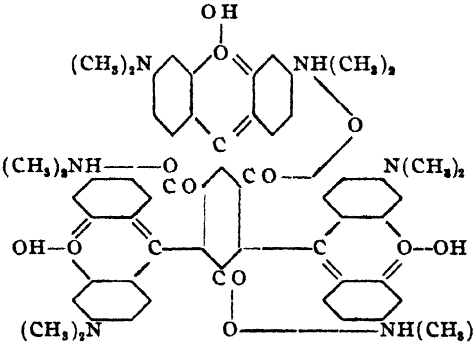
Of the two formulas, the balance of evidence is clearly in favor of a non-quinoidal structure, for there is no reason for assuming the anisolines to differ from the parent acids, the constitutions of which are fairly definitely settled below.

Constitution of the Rhodamines of Mellitic Acid.—In dealing with this subject it will be found simplest to consider the trixanthyl derivatives in the first place.

Hydrated dodecamethylhexaminotrihydroxytrixanthylbenzenetricarboxylactone may be regarded as typical. Of the many configurations it is possible to suggest on paper, we need seriously consider only two (VI and VII). The others will be found either to represent carboxylic acids, which may be rejected at once as the compound is a strong base, insoluble in caustic potash, or else, less satisfactory modifications of VI and VII.



VI.

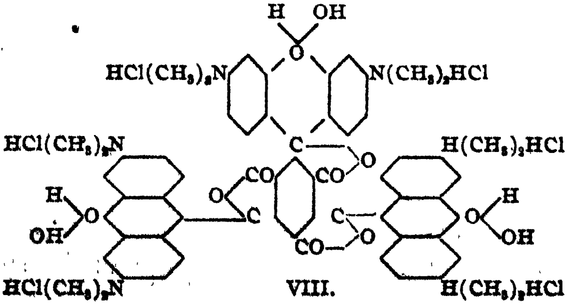


VII.

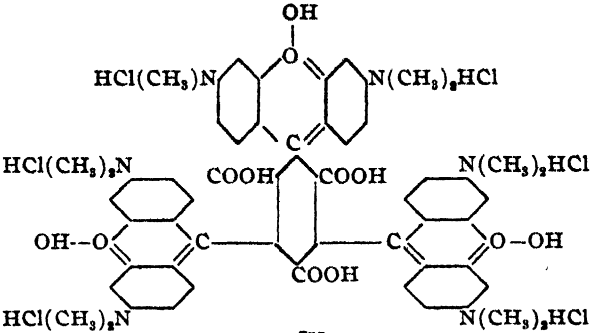
Hydrated dodecamethylhexaminotrihydroxytrixanthylbenzenetricarboxylactone.

The problem thus resolves itself into the question, Is this coloring matter a quinone or a lactone?

The compound is readily soluble in hydrochloric acid with formation of a hexahydrochloride without loss of water: formulating this salt on the two systems they assume the configurations represented by VIII and IX.



VIII.



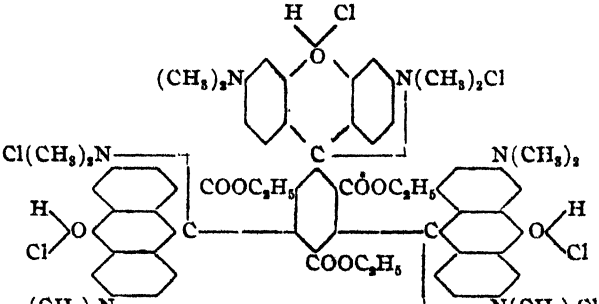
IX.

Hexahydrochloride of hydrated dodecamethylhexaminotrihydroxytrixanthylbenzenetricarboxylactone.

Of these two formula VIII is far the more probable. A free tricarboxylic acid such as represented by formula IX would scarcely form a hexahydrochloride; compare for instance the strongly acid character of the monoxanthyl derivatives which form pentabasic salts (I).

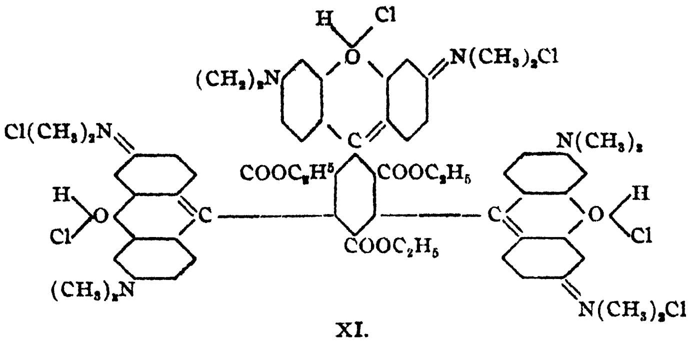
Further, anisolation can only be effected with extreme difficulty, whereas the dixanthyl derivatives, which are proved below to exist as inner salts, form anisolines with great readiness. This property must therefore be regarded as strong evidence in favor of the lactonic formula.

The anisoline chlorides combine with three molecules of hydrochloric acid forming trihydrochlorides of the trichlorides. These compounds can be formulated with equal readiness as lactones or quinones, X, XI.



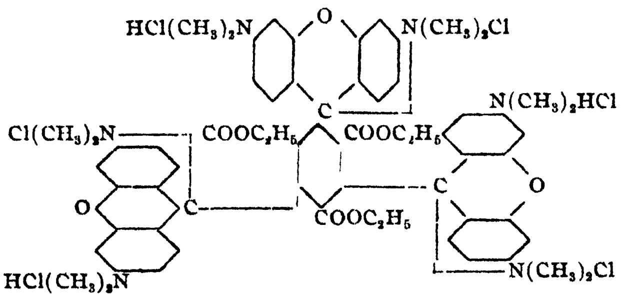
X.

Of the two formulas X is to be preferred, for although in this case the treatment required for anisolation is so drastic that the constitution may well have suffered alteration in the process, yet in the case of the dixanthyl compounds anisolation proceeds with the utmost ease: for this reason also the formula X is preferred to XII as well as to XI for the hydrochloride of the anisoline chloride; it is more strictly parallel with the most probable formula of the dixanthyl anisolines.



XI.

Trihydrochloride of anhydrododecamethylhexaminotrihydroxytrixanthylbenzenetricarboxylic ethyl ester trichloride.



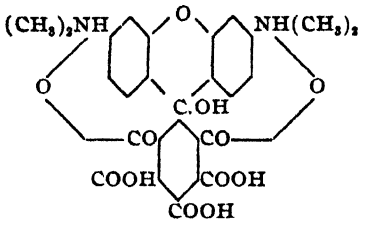
XII.

Hence this again must be regarded as an argument in favor of the lactonic formula.

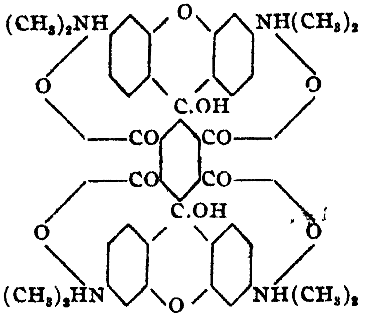
Action of Caustic Potash.—As already stated the compound is insoluble in caustic potash; heated with this reagent it slowly decomposes with evolution of dimethylamine. Such behavior is fairly conclusive evidence for the lactone formula. Indeed the possibility of an inner salt as represented by formula VII–IX withstanding the action of caustic potash in this manner is almost out of the question, especially when it is recollected that inner salts of the dixanthyl derivatives exhibit no such tendency, but dissolve immediately, forming tetrabasic salts (II and III).

It becomes evident therefore that the formula VI represents the constitution of hydrated dodecamethylhexaminotrihydroxytrixanthylbenzenetricarboxylactone, its hexahydrochloride being represented by formula VIII; while formula X most probably represents the constitution of the hydrochloride of the corresponding anisoline chloride.

Constitution of the Mono- and Dixanthyl Derivatives.—On carefully considering the properties of these derivatives in the light of the above arguments, it will become fairly evident that the parent compounds—for instance tetramethyldiaminohydroxyxanthylbenzenepentacarboxylic acid and octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylic acid—are to be regarded, not as hydrated lactones, but as inner salts, XIII and XIV.



XIII.



XIV.

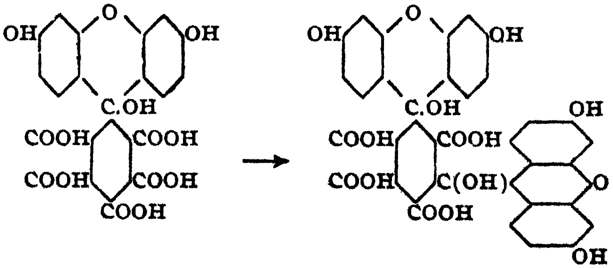
XIII. Tetramethyldiaminohydroxyxanthylbenzenepentacarboxylic acid.

XIV. Octamethyltetraminodihydroxyparadixanthylbenzenetetracarboxylic acid.

Anisolation, Action of Alkalies, Etc.—Unlike the trixanthyl derivatives these compounds anisolate with the greatest ease and dissolve at once in potash or ammonia, forming penta- and tetrabasic salts respectively (I and II). They can hardly therefore be regarded as hydrated lactones analogous to the trixanthyl compound which is insoluble in alkalies and readily dissolved in acids, but must be inner salts of true carboxylic acids.

The Formation of Dixanthyl Derivatives affords, perhaps, the most conclusive proof that the parent compounds are true inner salts.

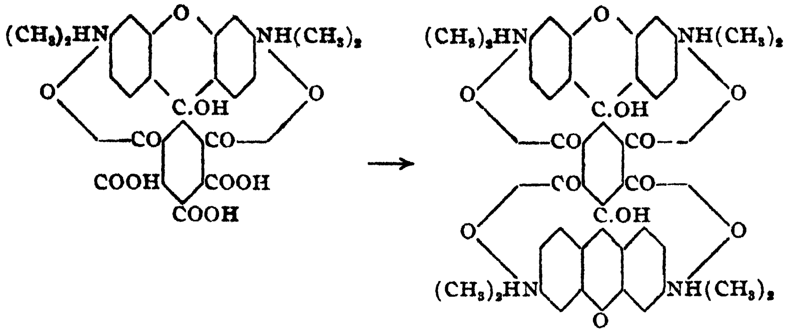
When mellitic acid is heated with four molecular proportions of resorcinol it was shown by one of the authors[1] that the monoxanthyl derivative first formed passed exclusively to the meta compound thus:



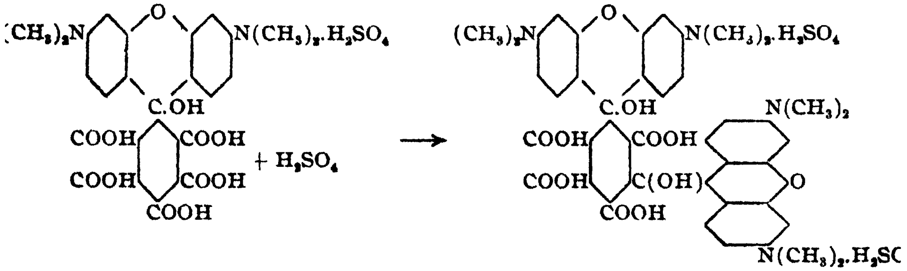
When, however, dimethylmetaaminophenol is substituted for resorcinol the para derivative is the sole product:

---

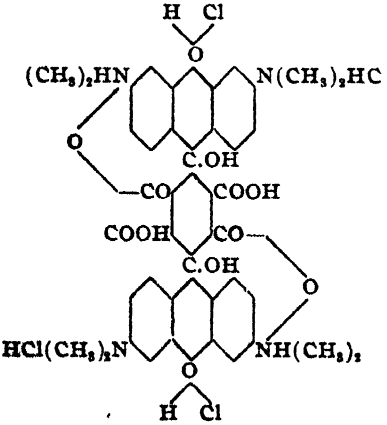
[1] *Loc cit.*



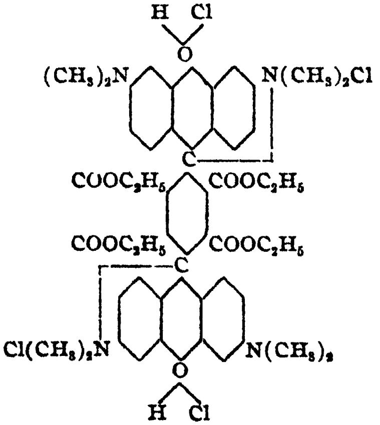
If, however, a small quantity of sulphuric acid be added the inner salt is broken up and the condensation proceeds in the normal manner with formation of the meta compound, the yield being almost theoretical:



From this it may be reasonably concluded that the parent compound exists as an inner salt.



XV.



XVI.

XV. Tetrahydrochloride of octamethyltetraminodihydroxydixanthylbenzene-tetracarboxylic acid.

XVI. Dihydrochloride of anhydro-octamethyltetraminodihydroxydixanthylbenzenetetracarboxylic ethyl ester dichloride.

The formation of a tetrahydrochloride of the acid (XV) and also the higher hydrochlorides of the anisolines (XVI) thus becomes a function of the latent property of the pyrone oxygen to become tetravalent.[1]

Lactones Isomeric but Not Tautomeric with Compounds of Quinonoid Structure.—In the previous work by one of the authors already referred to[2] indications were obtained that the lactone ring in these complex phthaleins shows much greater stability than has usually been attributed to it in compounds of this group. The present work has afforded additional evidence of this, for the trixanthyl derivatives, which must, as shown above, be regarded as lactones, are insoluble in alkalies but dissolve as lactones in acids (compare formulas VI and VIII), yielding solutions almost as strongly fluorescent as their corresponding anisolines, which, as has also been shown above, can be formulated with equal readiness either as quinonoid or carbinol derivatives (compare formulas X and XI). This has an important bearing on the theory of fluorescence of the phthalein group, which has generally been attributed to an oscillatory tautomerism between the lactone and quinonoid structures, inasmuch as it shows that no such oscillatory tautomerism can exist or account for the fluorescence of those compounds.

Orientation of the Xanthyl Groups in Aminodixanthyl Derivatives of Mellitic Acid.—As in the previous study of the resorcinol derivatives[2] the problem presented itself as to the relative positions of the xanthyl groups in the dixanthyl derivatives. As before, the method used for differentiating between the meta and the para position was to ascertain whether a third xanthyl group could be introduced.

Two isomeric dixanthyl derivatives are formed when mellitic acid is heated with dimethylmetaaminophenol, according as sulphuric acid is present or not. It is found that the compound prepared in presence of sulphuric acid is capable of taking up a third xanthyl group on heating with excess of dimethylmetaaminophenol, the resultant compound having the formula VI. Hence the dixanthyl compound from which this was prepared must have been a meta derivative, a salt of which is represented by formula III. When, however, mellitic acid and dimethylmetaaminophenol are heated together in absence of sulphuric acid, the product refuses to take up a third xanthyl group and is therefore the para compound, a salt of which is shown in formula II.

Since the para compound still contains two pairs of carboxylic groups ortho to one another, the non-formation of a trixanthyl derivative must be directly attributed to stearic hindrance, of which this thus forms one of the clearest examples on record.

Apart from this property the meta and para isomerides differ in other respects. Thus the octamethyltetraminodihydroxymetadixanthylbenzenetetracarboxylic acid is more readily anisolated than the para compound. In color also the two isomers show a marked difference.

---

[1] Compare Silberrad, *Proc. Chem. Soc.*, 24, 209 (1908).

[2] *Loc cit.*

Conclusions.

1. That, although it is conceivable that certain of these compounds—notably the anisolines—may possess a quinonoid structure, to represent them all as quinones, involves an absolute disregard for their properties and an indiscriminate introduction of the tetravalent oxygen irrespective of whether the presence of this element exercises a basic or acidic influence on the molecule.

2. That it may be regarded as fairly proved that *the presence of quinoidal grouping is not an essential integral part of a colored or fluorescent compound.*

Experimental Part.

In preparing the desired compounds the reacting ingredients were mixed in approximately molecular proportions and heated under widely varying conditions and the product from each experiment roughly purified and analyzed. A large quantity of the material was then prepared by that method which gave rise to the purest product. Final purification was, in most cases, effected by systematic fractional precipitation, samples being taken from time to time and analyzed; the fractionation was then again proceeded with until the analytical results became constant. In the execution of this work over four hundred analyses, the majority being nitrogen estimations, were carried out.

Monoxanthyl Derivatives.

3,6-Diamino-9-hydroxyxanthylbenzene-2-carboxylactone 3,4,5,6-Tetracarboxylic Acid (2 molecules metaaminophenol + 1 molecule mellitic acid), $C_{24}H_{14}O_{11}N_2$.

Preparation.—A finely powdered mixture of 6.84 parts mellitic acid and 4.32 parts metaaminophenol is heated to 160° for 8 hours. The resulting mass is ground and extracted with dilute aqueous caustic potash, the solution obtained filtered and the condensation product precipitated by acidification. The precipitate is filtered off, washed with boiling water, and then with alcohol, until the alcoholic washings are only slightly colored. The residue is purified by repeated fractional precipitation from an alkaline solution by the addition of dilute hydrochloric acid. The precipitate is finally boiled with a large volume of water, filtered and dried on a porous tile at 100°.

Calculated for $C_{24}H_{14}O_{11}N_2$:	N, 5.53.
Found (three different preparations):	N, 5.39, 5.55, 5.38.

Properties.—Light brown, amorphous powder, decomposing without melting above 300°. Insoluble in water, concentrated hydrochloric acid and nearly all organic solvents. Readily soluble in dilute alkalies giving a deep brown solution having a green fluorescence, precipitated from its solution on acidulation. Readily soluble in concentrated sulphuric acid, giving a brownish black solution, from which, on dilution, the acid is again precipitated. Fairly soluble in glacial acetic acid, giving a dark brown solution, from which the compound is precipitated on dilution.

Potassium Salt.—This is prepared by boiling an excess of the acid with dilute caustic potash, filtering off the excess and evaporating the neutral solution thus obtained to dryness. The salt separates out as a dark brown powder with a very dark bronzy metallic reflex; readily soluble in water, giving a deep brown solution.

Silver Salt, $C_{24}H_{10}O_{11}N_2Ag_4$.—This is precipitated as a dark brown powder on adding silver nitrate to a solution of the potassium salt. It is fairly stable to heat and light; is decomposed by dilute nitric and glacial acetic acids, the free acid being precipitated. It dissolves instantly in ammonia.

Calculated for $C_{24}H_{10}O_{11}N_2Ag_4$:	Ag, 46.25.
Found (two different preparations):	Ag, 46.35, 46.38.

The copper, barium, lead, ferrous and chromium salts form brown precipitates, while the cobalt, mercuric and ferric salts are reddish brown in color. The compound forms no definite hydrochloride.

Tetramethyl-3,6-diamino-9-hydroxyxanthylbenzenepentacarboxylic Acid (2 mols. dimethylmetaaminophenol + 1 mol. mellitic acid), $C_{28}H_{24}O_{12}N_2$.

Preparation.—A finely ground mixture of 6.2 parts mellitic acid and 5 parts dimethylmetaaminophenol is heated to 170° for 8 hours. During heating the mixture gradually solidifies, and on cooling forms a hard bronzy mass. This is powdered, boiled with water and then with alcohol to remove any unchanged acid or phenol. The condensation product is dissolved in dilute aqueous caustic potash, filtered and fractionally precipitated by the addition of hydrochloric acid. This treatment will be found insufficient to remove the impurities present. (The purest fraction from the fifteenth precipitation gave N = 5.17; $C_{28}H_{24}O_{12}N_2$ requires 4.84 per cent.) In order to obtain the pure compound, protracted extraction with alcohol followed by repeated fractional precipitation from its solution in dilute alkali by the addition of acid is necessary. In this way a pure compound is ultimately obtained.

Calculated for $C_{28}H_{24}O_{12}N_2$:	C, 57.90; H, 4.17; N, 4.84.
Found (three different preparations):	C, 57.68, 57.72; H, 4.24, 4.22; N, 4.94, 4.91, 4.95.

Properties.—Amorphous heliotrope-colored powder which decomposes, without melting, above 300°. Dyes silk and wool a silvery violet-pink. Insoluble in water, alcohol, chloroform, ether and ethyl acetate and only very slightly soluble in aniline and phenol. Slightly soluble in glacial acetic acid from which solution it is precipitated on dilution with water. Soluble in concentrated hydrochloric and sulphuric acids giving brown solutions; on dilution the pink color returns and the acid is for the most part precipitated unaltered. Readily soluble in dilute caustic potash and ammonia, giving dark red solutions having a brown fluorescence; from these solutions the compound is precipitated on acidulation.

The Potassium Salt is prepared by boiling an excess of the acid with dilute alkali, filtering off the excess and evaporating the neutral solution to dryness. The salt forms a dark violet-red powder having a dark violet reflex. It is very soluble in water and its solution fluoresces strongly.

The Silver Salt $C_{28}H_{10}O_{12}N_2Ag_5$ is precipitated as a dark blood-red precipitate, which when dry has a dark reddish brown color and is remarkably stable to light. Dissolves instantly in ammonia. Dilute nitric and glacial acetic acids dissolve the salt and precipitate out the acid.

Calculated for $C_{28}H_{10}O_{12}N_2Ag_5$: Ag, 48.43.
Found (two different preparations): Ag, 48.67, 48.59.

The copper, cobalt, ferric and ferrous salts are precipitated as reddish brown powders, while the barium and chromium salts are blood-red precipitates. The compound forms no definite hydrochloride. On evaporating its solution in concentrated hydrochloric acid the residue retains only traces of chlorine, which it slowly loses over quicklime.

Tetramethyl-3,6-diamino-9-hydroxyxanthylbenzenepentacarboxylic Ethyl Ester Chloride, $C_{38}H_{43}O_{11}N_2Cl$.

Preparation. — Tetramethyl-1,3,6-diamino-9-hydroxyxanthylbenzene pentacarboxylic acid is suspended in absolute alcohol and dry hydrochloric acid gas passed through the liquid, until nearly all the acid has gone into solution. The mixture is evaporated to dryness on the water bath and the residue extracted with alcohol. The unchanged acid is filtered off and the filtrate evaporated to dryness, and finally purified by repeated fractional precipitation.

Calculated for $C_{38}H_{43}O_{11}N_2Cl$: N, 3.79; Cl, 4.80.
Found (three different preparations): N, 3.96, 3.67, 3.65; Cl, 5.16, 4.98, 4.61.

Properties. — Dark violet-red, amorphous powder, having a bronzy metallic reflex. Dyes silk and wool a violet-red. Insoluble in ether, benzene and chloroform. Very slightly soluble in water, acetone, ethyl acetate and concentrated hydrochloric acid, giving fine deep pink solutions. Readily soluble in phenol, aniline, glacial acetic acid and alcohol in which last it gives a deep violet-red solution having an intense brown fluorescence. Readily soluble in concentrated sulphuric acid, giving a brown solution which on dilution becomes red. In strong, cold, caustic potash and ammonia it is slightly soluble, giving deep violet-red solutions having a brown fluorescence.

Hydrochloride of Tetramethyldiaminohydroxyxanthylbenzenepentacarboxylic Ethyl Ester Chloride, $C_{38}H_{44}O_{11}N_2Cl_2$.

Preparation.—On evaporating the pure anisoline chloride described above with hydrochloric acid the ester takes up another molecule of hydrochloric acid. The compound is purified by exposure over quicklime until it becomes constant in weight.

Calculated for $C_{38}H_{44}O_{11}N_2Cl_2$: Cl, 9.03.
Found: Cl, 8.5.

Properties.—Dark reddish powder possessing a bronzy reflex. On treatment with water it loses one molecule of hydrochloric acid with formation of the anisoline chloride.

Tetraethyl-3,6-diamino-9-hydroxyxanthylbenzenepentacarboxylic Acid (2 mols. diethylmetaaminophenol + 1 mol. mellitic acid), $C_{32}H_{32}O_{12}N_2$.

Preparation.—A finely ground mixture of six parts mellitic acid and 5 parts diethylmetaaminophenol is heated to 170° for 5 hours. The mass on cooling is dissolved in dilute caustic potash, filtered, and the condensation product precipitated by means of hydrochloric acid, filtered off, washed with boiling water, then with alcohol, and purified by repeated fractional precipitation of its alkaline solution by the addition of acid. The compound is then freed from salt which it tenaciously retains, by extraction with water.

Calculated for $C_{32}H_{32}O_{12}N_2$: N, 4.41.
Found (two different preparations): N, 4.48, 4.39.

Properties.—Dull red heliotrope, amorphous powder, which decomposes without melting above 300°. Dyes silk and wool a silver gray pink. In its solubility and other properties, it is practically identical with the tetramethyl compound.

Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxy-m-dixanthylbenzene-2,4,5,6-tetracarboxylic Acid (4 mols. dimethylmetaaminophenol + 1 mol. mellitic acid), $C_{44}H_{42}O_{12}N_4$.

Preparation.—6.84 parts of mellitic acid and 11 parts dimethylmetaaminophenol are finely ground together and heated to 165–170° with 4 parts concentrated sulphuric acid for 6 hours. The mixture gradually solidifies. On cooling, the mass is ground, boiled out thoroughly with water and the residue dissolved in dilute alkali. The solution is filtered and the condensation product precipitated by means of acid. The product is then well washed with boiling water, then with alcohol to remove unchanged dimethylaminophenol, and purified by repeated fractional precipitation from its potassium salt by means of acid.

Calculated for $C_{44}H_{42}O_{12}N_4$: C, 64.50; H, 5.17; N, 6.86.
Found (three different preparations): C, 64.34, 64.42, 64.36; H, 5.16, 5.31, 5.17; N, 6.76, 6.85, 6.72.

Properties.—Bright violet-red, amorphous powder, much brighter than the para isomeride. Decomposes without melting above 300°. Dyes silk and wool a violet-red; is insoluble in water, alcohol, chloroform, ethyl acetate, ether and acetone Fairly soluble in phenol and aniline. Readily soluble in concentrated sulphuric, hydrochloric and acetic acids, from [illegible] precipitated on being largely diluted. Very soluble [illegible] and ammonia, giving a deep violet-red solution, [illegible] ence, precipitated on acidification.

[illegible] and lithium salts are dark brownish violet powders with [illegible] metallic reflex Very soluble in water, forming deep bright violet red solutions having an intense brown fluorescence.

Silver Salt, $C_{44}H_{38}O_{12}N_4Ag_4$ – Is a dark violet-red powder, with a dark violet red reflex Is extremely stable to light and heat and dissolves instantly in ammonia Dilute nitric and acetic acids dissolve the salt but precipitate out the acid

Calculated for $C_{44}H_{38}O_{12}N_4Ag_4$	Ag, 34 65
Found (two different preparations)	Ag, 34 51, 34 66

The copper, barium, cobalt, ferric, ferrous, chromium and mercuric salts are formed as bright violet red precipitates, the copper and barium salts being unaltered by ammonia.

Tetrahydrochloride of Octamethyl-3,3',6,6'-tetramino-9,9'-dihydroxymetadixanthylbenzene 2,4,5,6-tetracarboxylic Acid, $C_{44}H_{46}O_{12}N_4Cl_4$

Preparation -The aforementioned acid is dissolved in concentrated hydrochloric acid and the solution evaporated to dryness on the water bath and allowed to stand over quicklime until a constant weight is reached

Calculated for $C_{44}H_{45}O_{12}N_4Cl_4$	Cl, 14 73
Found (three different preparations)	Cl, 15 00, 14 97, 14 95.

Properties — Dark reddish powder possessing a metallic reflex, which when dissolved in water suffers hydrolysis, the acid being precipitated practically free from chlorine. Under no conditions could a compound containing two molecules of hydrochloric acid be obtained.

[illegible] *mino-9,9'-dihydroxymetadixanthylbenzene - 2,4,5-* [illegible] *er Dichloride*, $C_{52}H_{58}O_{10}N_4Cl_2$.

[illegible] oing acid is suspended in alcohol and dry hydro-[illegible] acid gas [illegible] through the mixture. The acid rapidly passes into solution with evolution of heat. In order to obtain the pure compound it is advisable to stop the current of gas just before all the acid is esterified. The mixture is then evaporated to dryness, the residue extracted with alcohol and the alcoholic extract precipitated by the addition of water.

Calculated for $C_{52}H_{56}O_{10}N_4Cl_2$:	N, 5.73; Cl, 7.27.
Found (two different preparations):	N, 5.98, 5.81; Cl, 7.27, 7 43.

Properties.—Dark violet-red amorphous powder having a bright bronzy reflex. On rapid heating it softens at 169–170°. Dyes silk and wool a reddish violet. Insoluble in ether, water, acetone, benzene, chloroform and ethyl acetate. Readily soluble in phenol, glacial acetic acid and aniline, giving bright violet-red solutions. Readily soluble in concentrated sulphuric and hydrochloric acids, giving brown solutions which turn red on dilution. Readily soluble in alcohol and precipitated therefrom on dilution with water.

Dihydrochloride of Octamethyl-3,3′,6,6′-tetraminometadixanthylbenzene-2,4,5,6-tetracarboxylic Ethyl Ester Dichloride, $C_{52}H_{58}O_{10}N_4Cl_4$.

Preparation.—An alcoholic solution of the aforementioned anisoline is saturated with hydrochloric acid, evaporated to dryness and exposed over quicklime until the weight becomes constant.

Calculated for $C_{52}H_{58}O_{10}N_4Cl_4$: Cl, 13.65.
Found (two different preparations): Cl, 13.80, 13.88.

Properties.—Dark reddish powder possessing a bronzy reflex. On treatment with water it at once loses 2 molecules of hydrochloric acid with the formation of the anisoline dichloride.

Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxymetadixanthylbenzene-2,4,5,6 tetracarboxylic Benzyl Ester, $C_{72}H_{66}O_{12}N_4$.

Preparation.—The potassium salt of octamethyltetraminodihydroxy-*m*-dixanthylbenzene-2,4,5,6-tetracarboxylic acid is suspended in alcohol, excess of benzyl iodide added, and the mixture heated to 130° for 8 hours. The colored solution is filtered, the residue washed thoroughly with boiling absolute alcohol, and the filtrate and washings evaporated to dryness on the water bath. The ester is purified by redissolving in alcohol, evaporating to dryness, and warming to 100° *in vacuo* to remove the excess of benzyl iodide; it is then again dissolved in alcohol and fractionally precipitated by the addition of water.

Calculated for $C_{72}H_{66}O_{12}N_4$: N, 4.76.
Found (two different preparations): N, 4.89, 4.65.

Properties.—The benzyl ester is a bright reddish violet, amorphous powder, having a dark violet-red metallic reflex. On rapid heating it melts and froths up at 147°. Dyes silk and wool a fine reddish mauve color. Insoluble in water, ether, benzene, caustic potash and ammonia. Slightly soluble in ethyl acetate and chloroform. Readily soluble in alcohol, aniline, acetone, phenol, and glacial acetic acid, the last giving a deep red colored solution having an intense brown fluorescence. Readily soluble in concentrated sulphuric acid with a reddish brown coloration which turns much redder on dilution.

Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxyparadixanthylbenzene-2,3,5,6-tetracarboxylic Acid (4 mols. dimethylmetaaminophenol + 1 mol. mellitic acid), $C_{44}H_{42}O_{12}N_4$.

Preparation.—10.25 parts mellitic acid and 19.4 parts of dimethylmetaaminophenol are finely ground together and heated to 160° for 8 hours. On commencing the heating the phenol melts but subsequently the whole gradually solidifies and the reaction is completed in about 8 hours.

When cold the mass, which has a bronzy metallic glance, is powdered and the condensation product together with the unchanged phenol is extracted with dilute aqueous caustic potash. The solution is filtered and the products are precipitated by acidifying with hydrochloric acid. The precipitate is filtered off, washed very thoroughly with boiling water, then with alcohol till the washings are scarcely colored, and finally purified by repeated fractional precipitation of its potassium salt by means of dilute acid. This it will be found is insufficient to produce a pure product, it being necessary subsequently to extract for at least 2 hours with alcohol and then dry at 80° on a porous tile.

Calculated for $C_{44}H_{42}O_{12}N_4$:	C, 64.50, H, 5.17; N, 6.86.
Found (two different preparations):	C, 64.35, 64.64; H, 5.05, 5.00; N, 6.83, 6.93.

Properties.—Dark reddish violet, amorphous powder. Decomposes without melting above 300°. Dyes silk and wool a silvery pink. Insoluble in water, alcohol, chloroform, ethyl acetate and ether. Slightly soluble in aniline, phenol, glacial acetic acid from which last solution it is precipitated on dilution with water. Very soluble in dilute alkalies, precipitated on acidification. In concentrated hydrochloric and sulphuric acids it is readily soluble without decomposition, and is precipitated on addition of water.

Salts.—The potassium and lithium salts are dark violet-red powders, having a dark violet-red reflex. They dissolve readily in water, giving fine violet-red solutions which show a marked brown fluorescence in concentrated solution.

Silver Salt, $C_{44}H_{38}O_{12}N_4Ag_4$, is precipitated as a dull red precipitate which is very stable to light and heat. It is readily soluble in ammonia. Dilute nitric and acetic acids dissolve the salt with precipitation of the free acid.

Calculated for $C_{44}H_{38}O_{12}N_4Ag_4$:	Ag, 34.65.
Found (four different preparations):	Ag, 34.67, 34.79, 34.52, 34.48.

The copper, cobalt, lead, ferrous and chromium salts are precipitated as deep red powders, while the barium salt is a blood-red precipitate.

The ferric salt is as a reddish brown, gelatinous precipitate.

Tetrahydrochloride of Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxyparadixanthylbenzene-2,3,5,6-tetracarboxylic Acid, $C_{44}H_{40}O_{12}N_4Cl_4$.

Preparation.—A solution of the acid in strong hydrochloric acid is evaporated just to dryness on the water bath; and then exposed over quicklime until its weight becomes constant.

Calculated for $C_{44}H_{46}O_{12}N_4Cl_4$: Cl, 14.73.
Found (two different preparations): Cl, 14.51, 14.55.

Properties.—Dark reddish powder possessing a metallic reflex, which, when dissolved in water, evidently suffers hydrolysis, the acid being reprecipitated practically free from chlorine. Under no circumstances could a compound containing 2 HCl be obtained.

Octamethyl - 3,3,'6,6' - tetramino - 9,9' - dihydroxyparadixanthylbenzene - 2,3,5,6-tetracarboxylic Ethyl Ester Dichloride, $C_{52}H_{56}O_{10}N_4Cl_2$.

Preparation.—The corresponding acid is suspended in alcohol and dry hydrochloric acid gas passed slowly through the solution. During this process the temperature rises; the gas is passed through the mixture until solution is almost complete. The product is then evaporated to dryness, the residue extracted with alcohol, and the alcoholic extract evaporated on the water bath and purified by fractional precipitation.

Calculated for $C_{52}H_{56}O_{10}N_4Cl_2$: N, 5.73; Cl, 7.27.
Found (two different preparations): N, 5.62, 5.90, 5.84; Cl, 7.46, 7.52.

Properties.—Dark reddish violet, amorphous powder, having a bronzy metallic reflex. On rapid heating the substance begins to froth up at 138°. Dyes silk and wool a violet-red. Insoluble in ether, benzene, chloroform and ethyl acetate. Very slightly soluble in water and acetone. Readily soluble in phenol, aniline, glacial acetic acid and alcohol, giving deep violet-red solutions having an intense brown fluorescence. Readily soluble in concentrated sulphuric acid and hydrochloric acid, giving a brown solution from which the compound is precipitated on dilution with water.

Dihydrochloride of Octamethyl-3,3',6,6'-tetraminoparadixanthylbenzene-2,4,5,6-tetracarboxylic Ethyl Ester Dichloride, $C_{52}H_{58}O_{10}N_4Cl_4$.

Preparation.—An alcoholic solution of the corresponding anisoline is saturated with hydrochloric acid gas, evaporated to dryness and exposed over quicklime until the weight becomes constant.

Calculated for $C_{52}H_{58}O_{10}N_4Cl_4$: Cl, 13.65.
Found (two different preparations): AgCl, 13.29, 15.69.

Properties.—Dark reddish powder possessing a bronzy reflex. On treatment with water it at once loses two molecules of hydrochloric acid with formation of the anisoline dichloride.

Octaethyl - 3,3',6,6' - tetramino - 9,9' - dihydroxyparadixanthylbenzene - 2,3,5,6-tetracarboxylic Acid (4 mols. diethylmetaaminophenol + 1 mol. mellitic acid), $C_{52}H_{58}O_{12}N_4$.

Preparation.—This is prepared by heating 8 parts diethylmetaaminophenol with 6 parts mellitic acid to 160° for 6 hours. The unaltered diethylmetaaminophenol is dissolved out by means of alcohol, and the condensation product purified by repeated fractional precipitation from its potassium salt by the addition of dilute acid.

Calculated for $C_{52}H_{58}O_{12}N_4$: N, 6.03.
Found (two different preparations): N, 6.00, 6.17.

Properties.—Light violet-red, amorphous powder. Decomposes without melting above 300°. Dyes silk and wool a silvery violet-red. General properties similar to those of the octamethylparadixanthyl compound.

Tetramethyl - 3,6 - diaminotetraethyl - 3′,6′ - diamino-9,9′ - dihydroxymeta - dixanthylbenzene-2,4,5,6-tetracarboxylic Acid (2 mols. diethylmetaaminophenol + 2 mols. diethylmetaaminophenol + 1 mol. mellitic acid), $C_{48}H_{50}O_{12}N_4$,

Preparation.—This is prepared by heating a mixture of tetraethyldiaminohydroxyxanthylbenzenepentacarboxylic acid and dimethylmetaaminophenol in the proportion of 1 molecule of the former to two of the latter with sulphuric acid to 170° for 6 hours. Water is then added to the mixture and the condensation product filtered off and purified in the usual manner.

Calculated for $C_{48}H_{50}O_{12}N_4$: N, 6.42.
Found (two different preparations): N, 6 49, 6.33.

Properties.—Dark violet-red, amorphous powder decomposing above 300° without melting. Dyes silk and wool a violet-red color. In its general properties it closely resembles the octamethylmetadixanthyl compound.

Orientation of the Two Isomeric Dixanthyl Derivatives.—In order to determine the relative position of the two xanthyl groups the two octamethyl isomers were further heated with excess of dimethylmetaaminophenol to 200°. In the case of the para compound (prepared in the absence of sulphuric acid) no trixanthyl derivative was formed. The result was similar when this compound was heated for 12 hours to 170° with dimethylmetaaminophenol and concentrated sulphuric acid, 80 per cent. of the original dixanthyl compound being recovered in a pure state and the residue was proved to be free from trixanthyl derivatives. The xanthyl groups therefore occupy para positions in the compound produced by heating mellitic acid with 4 or more molecular proportions of dimethylmetaaminophenol in the absence of sulphuric acid. This, it is interesting to note, is contrary to the behavior of the hydroxyxanthyl derivatives dealt with in a previous paper (*J.Chem.Soc.(London)*, 89, 1760).

The compound above described as octamethyltetraminometadixanthylbenzenetetracarboxylic acid, produced by condensing mellitic acid with dimethylmetaminophenol in the presence of sulphuric acid, readily combines with another molecular proportion of the aminophenol with production of the trixanthyl derivatives described below.

Dodecamethyl - 3,3′,3′′,6,6′,6′′ - hexamino - 9,9′,9′′ - trihydroxy - sym - tri - xanthylbenzene-2,4,6-tricarboxylactone (6 mols. dimethylmetaaminophenol + 1 mol. mellitic acid), $C_{60}H_{60}O_{12}N_6$.

Preparation.—All early attempts to obtain this compound were fruitless owing to the fact that unlike the resorcinol compounds previously studied[1] direct heating of the mixture of aminophenol and mellitic acid leads to the production of the para dixanthyl derivatives. Thus varying excesses of aminophenol were heated with mellitic acid to temperatures ranging from 160 to 200° for times varying from 8 to 18 hours, both alone and subsequently in the presence of small quantities of sulphuric acid; in the latter instances small quantities of a trixanthyl compound were obtained which ultimately led to the following method of preparation.

Twenty-five parts mellitic acid were finely ground up with 62 parts dimethylmetaaminophenol, 100 parts concentrated sulphuric acid added and the whole gradually heated up to 180° and maintained at that temperature for 8 hours. After cooling, water is added to the black mixture and the whole warmed till the product is almost all dissolved. The solution is then filtered and the filtrate precipitated by the addition of a slight excess of alkali. The precipitate is then repeatedly washed, but, owing to the impervious and slime-like nature great difficulty is experienced in purifying the compound. At this stage, after drying at 100°, one preparation gave on analysis 8.6 per cent. N (required by $C_{60}H_{60}O_{12}N_6$ 7.95); after extraction with alcohol for several days in a Soxhlet it was found to contain 8.25 per cent. The product was therefore repeatedly boiled for several hours with large quantities of water, allowed to settle over night and the aqueous liquor decanted off. This treatment was then repeated with alcohol until the supernatant liquor is but faintly colored, after which the residue was finally filtered off and dried at 90°.

Calculated for $C_{60}H_{60}O_{12}N_6$: C, 68.18; H, 5.68; N, 7.95.
Found (three different preparations): C, 68.30, 67.95, 68.00; H, 5.53, 5.75, 5.53; N, 7.97, 7.88, 8.04, 7.97.

Properties.—Dark violet-brown, amorphous powder, which decomposes without melting above 300°. Dyes silk and wool a pale silver pink. Insoluble in water, alcohol, chloroform, acetone, ether, benzene, ethyl acetate and ammonia. Slightly soluble in glacial acetic acid, readily soluble in phenol giving a deep red solution. Readily soluble in concentrated sulphuric and hydrochloric acids, giving a brownish red solution which on dilution becomes red. The compound is insoluble in caustic potash; boiling with a 40 per cent. solution causes slight decomposition with evolution of dimethylamine.

Hexahydrochloride of Dodecamethyl-3,3′,3′′,6,6′,6′′-hexamino-9,9′9′′-trihydroxy-sym-trixanthylbenzene-2,4,6-tricarboxylactone, $C_{60}H_{66}O_{12}N_6Cl_6$.

Preparation.—The above lactone is dissolved in concentrated hydrochloric acid, and the solution evaporated to dryness on the water bath; the residue is then exposed over quicklime until a constant weight is reached.

---

[1] *Loc. cit.*

Calculated for $C_{60}H_{66}O_{12}N_6Cl_6$: Cl, 16.70.
Found (two different preparations): Cl, 16.96, 16 90, 16.34, 16.47.

Properties.—Dark bronzy powder. Soluble in water with gradual precipitation of the base; boiling accelerates the hydrolysis. The precipitated base is practically free from chlorine; the compound shows no tendency to produce a trichloride.

Dodecamethyl-3,3′,3″,6,6′,6″-hexamino-9,9′,9″-trihydroxy-sym-trixanthylbenzene-2,4,6-tricarboxylic Ethyl Ester Trichloride, $C_{66}H_{69}O_9N_6Cl_3$.

Preparation.—This is prepared by dissolving the foregoing acid in concentrated hydrochloric acid, precipitating the hydrochloride by means of absolute alcohol and then heating the finely divided hydrochloride thus obtained in a sealed tube with excess of alcoholic hydrochloric acid to 140°. The residue is filtered off and the alcoholic solution evaporated to dryness on the water bath, the residue being purified by repeated fractional precipitation of its alcoholic solution by means of water.

Calculated for $C_{66}H_{69}O_9N_6Cl_3$: N, 7.02.
Found (two different preparations): N, 7.11, 7.11.

Properties.—Dark violet-brown, amorphous powder having a dark metallic reflex. Decomposes without melting above 300°. Dyes silk and wool a pinkish mauve. Insoluble in chloroform, acetone, ether, benzene, ethyl acetate, glacial acetic acid, aqueous alkalies and water. Fairly soluble in alcohol, giving a deep red solution having a brown fluorescence. Readily soluble in phenol and aniline, giving red-brown solutions. Readily soluble in concentrated sulphuric and hydrochloric acids, giving red-brown solutions which on dilution assume a fine red; and from which the ester is precipitated by alkalies.

Trihydrochloride of Dodecamethyl-3,3′,3″,6,6′,6″-hexamino-9,9′,9″-trihydroxy-sym-trixanthylbenzene-2,4,6-tricarboxylic Ethyl Ester Trichloride, $C_{66}H_{72}O_9N_6Cl_6$.

Preparation.—An alcoholic solution of the corresponding anisoline is saturated with hydrochloric acid evaporated to dryness and exposed over quicklime until the weight becomes constant.

Calculated for $C_{66}H_{72}O_9N_6Cl_6$: Cl, 16.32.
Found (two different preparations): Cl, 16.00, 16.08.

Properties.—Dark reddish powder possessing a violet-bronzy reflex soluble in alcohol from which solution water precipitates the trichloride.

In conclusion we desire to express our gratitude to Messrs. Read Holliday & Sons of Huddersfield, England and Brooklyn, U. S. A., for permission to publish this work and also for supplying much of the *mellitic acid* required in its execution.

THE SILBERRAD RESEARCH LABORATORIES,
BUCKHURST HILL, ESSEX, ENGLAND,
AND 27 CHANCERY LANE, LONDON, W. C.

THE STIMULATION OF PREMATURE RIPENING BY CHEMICAL MEANS.

BY A. E. VINSON.

Received December 3, 1909.

Artificial ripening of persimmons, dates and other fruits has been practiced for many years, but some particular substance has always been deemed essential, such as the empty *sake* barrel for persimmons or cloths moistened with vinegar for dates. Analogous to this and probably due to similar biochemical phenomena is the forcing of buds to open prematurely by what is supposed to be anesthetization, or by the application of heat as shown by Molisch.[1] The premature sprouting of newly formed tubers by stimulation with divers chemicals, which has been accomplished recently by McCallum,[2] belongs to this same general class of phenomena. Many plants[3] which contain certain glucosides and emulsin show an abnormally large exhalation of hydrocyanic acid or other substances after treatment with anesthetics and other poisonous vapors or by freezing, and this is accompanied by marked plasmolysis.

For a critical study of the influence of chemicals in initiating the premature ripening of fruits, a tree of particularly well adapted seedling dates was available. The fruits were light yellow when unripe and indicated their start to ripen by the appearance of a well-marked translucency, which increased and darkened until they became a deep chocolate-brown. The effect of over one hundred separate substances was studied on this material, either by exposing the fruits to the vapor of the volatile ones or by soaking them in solutions of the nonvolatile compounds.

The first results[4] seemed to indicate that the effect was dependent on chemical structure, since certain groups gave very marked results while others did not. Acetic acid and acetic ether were equally efficient, and five per cent. solutions of sodium or potassium acetate also gave good results. Aniline acetate vapor acted slowly but perfectly. Solutions of both benzoic and salicylic acids acted very promptly and completely. Oxalic acid gave marked results but malonic and succinic acids appeared to act much better. Citric, tartaric, and malic acids gave only imperfect results. In the first trials ordinary ether, chloroform and acetone failed, but it was found later that dates responded only to nearly saturated vapors of these reagents. Many substances which are not easily volatile acted quickly by direct contact but very slowly by their vapors. In general the more volatile the substance the quicker it acted; thus benzene and toluene acted very completely over night, but xylene, in the same time, affected only the bottom of the column of fruit above it, the effect traveling slowly upward. Oil of eucalyptus acted quite readily, while pennyroyal and cassia were very slow excepting by contact. Eugenol acted quickly by contact but its vapor was without effect even after many days' exposure. Camphor and naphthalene were not sufficiently volatile to give any result. Among the more peculiar results were those obtained with iodoform. With this substance the entire column turned uniformly, there being no difference between the fruits in actual contact and those farther away.

---

[1] "Das Warmbad als Mittel zum Treiben der Pflanzen," Jena, 1909.

[2] Unpublished work, Arizona Agr. Exp. Station.

[3] Mirande, *Compt. rend.*, 149, 140; Guignard, *Compt. rend.*, 149, 91.

[4] *Science*, 30, 604 (1909).

A detailed account of the action of the various substances used, grouped according to their efficiency, is given below:

Fruits turned uniformly throughout the column over night by saturated vapors of the following:

Ether, chloroform, acetone, gasoline, carbon disulphide, benzene, toluene, allylisosulphocyanate, ethyl and methyl alcohols (a little slow, methyl alcohol acting better), ethyl acetate, ethyl butyrate, ethyl oxalate, ethyl chloride, ethyl bromide, acetyl chloride (not in excess), ethylene chloride (very efficient), methyl dichloride (very efficient), amyl formate, amyl acetate, acetic acid, propionic acid, butyric acid and acetal.

Fruits turned uniformly over night but farther ripening did not proceed normally with saturated vapors of:

Formaldehyde, acetaldehyde, formic acid, methyl acetate and ethyl formate. Possibly some of these would have been efficient in less concentration since excess probably interfered with the action of the enzymes.

Fruits ripened by contact over night, those above ripening in the next 24 to 48 hours:

Xylene, amyl alcohol, isobutyl alcohol, diacetic ester, benzyl chloride, benzoyl chloride, chloral, ethyl succinate, ethyl benzoate, cumene, cymene, geraniol, citral, coal oil, turpentine.

Fruits ripened by contact in the first few days; those above ripened only after prolonged exposure to vapor:

Mono-, di- and trichloroacetic acids, monobromoacetic acid, aniline acetate, pyridine, toluidine, oil of eucalyptus, benzaldehyde, hypnone, iodoform (by contact and by vapor ripening at the same time), terpineol.

Fruits ripened by contact only:

Aniline, phenolhydrazine, thymol, oil of cassia and oil of pennyroyal.

Fruits not affected:

Camphor, naphthalene, menthol, hydrochloric acid; blackened and destroyed by phenol; damaged but not ripened by chloral hydrate and sulphur dioxide.

Ethyl and amyl nitrite penetrate very rapidly and react chemically with the content of the tannin cells, causing it to precipitate and form insoluble tannin grains at once.[1] Due to the darkening of the fruit the effect on ripening other than the removal of astringency is difficult to follow. In smaller quantities it appears to stimulate the other ripening phenomena and very palatable fruits can be prepared by the use of nitrous esters. Ammonia in small quantities causes a general reddening of the fruits with shrinking at the basal end. The general ripening phenomena follow fairly well and after some days the fruits are edible.

The stimulation due to solutions was not so easily traced as that due to vapors. The first effect usually manifested itself by the appearance of translucent spots instead of the fruit turning as a whole. Many substances caused the skin to crack and curl badly, sometimes accompanied by ripening, sometimes not. Saturated solutions of benzoic and salicylic acids over night produced first effects very similar to those produced by vapors, while malonic, succinic and lactic acids in three per cent. solutions and the acid amides were almost equally efficient.

The following substances in solution caused all or nearly all the treated fruits to ripen:

Benzoic acid, salicylic acid, sodium benzoate, sodium salicylate, sodium acetate, potassium acetate, oxalic, malonic and succinic acids, lactic acid, acetamide, formamide, hippuric acid, cinnamic acid, hydroxylamine hydrochloride; hydrazine hydrochloride starts the process but normal ripening does not follow.

The following substances ripen from one-half to two-thirds of the fruits treated:

Tartaric, citric and malic acids, trichloroacetic acid (one-tenth per cent. solution), ammonium acetate, manganese sulphate and aniline acetate.

The following gave doubtful or negative results:

Potassium sulphate, manganese chloride, sulphanilic acid, acetanilide, phenacetine, protocatechuic acid, pyrogallol, orcinol, resorcinol and vanillin.

From the diversity of these reagents it is evident that the effects observed cannot be due to any particular chemical structure, nor do many of them react chemically with any known constituent of the date. Furthermore, after treatment over night with acetic acid vapor, an appreciable reaction for invertase could be obtained in the glycerol extract although a marked astringency was still present. From these facts and previous work on the intracellular invertase of the date,[2] including some recent observations[3] on the chemical organization of the green fruit while it retained its physical integrity, it was concluded that this apparent stimulation of ripening depended solely on the killing of the protoplasm. In broad terms any substance which will penetrate the cuticle and kill or stimulate the protoplasm, thereby releasing the previously insoluble intracellular enzymes without rendering them inactive, will bring about ripening, provided the fruits have reached a certain necessary degree of maturity.

---

[1] *Bot. Gaz.* The work is now in process of publication.

[2] THIS JOURNAL, 30, 1005 (1908).

[3] *Plant World*, Jan., 1910.

The validity of this theory was tested by an experiment devised to accomplish the same results by purely physical means. Sprays of dates were heated in water for five and ten minutes at every five degrees between 60 and 95°. Below 60° they lost their astringency but remained very light colored like untreated fruits. Above 60° the color became darker, reaching a maximum at about 75°. At 80° the general aspect of the sprays was more uneven, and even the darkest individuals remained exceedingly astringent and very sweet. Above 80° the color of the entire sprays became very light, matching exactly the more immature individuals heated below 60°. Unlike the results obtained by treatment with chemicals, the effects of heat stimulation become plainly manifest only after the lapse of several days. The results, however, show clearly that if dates are heated sufficiently to destroy protoplasm but not enzymes, the ripening phenomena will follow quite completely, while at higher temperatures all ripening ceases.

Apsit and Gain[1] have shown that seeds lose their viability when subjected to anesthetics for a considerable length of time but their diastase and peroxydase remain active. In this case as in others, anesthesia in the accepted meaning of the word has nothing to do with the effects produced. The only connection is that certain substances, among many others, which kill or stimulate the protoplasm happen to produce anesthesia in animals.

The more immature fruits heated to 70° for ten minutes or longer darkened nicely but remained astringent. At higher temperatures even the more mature fruits remained permanently astringent while untreated immature fruits gradually lost their astringency. These facts can be explained only as the direct or indirect action of some specific enzyme that is destroyed at about 70°. Hydrazine hydrochloride interfered with the general trend of ripening but the astringency disappeared.

Commercially, many varieties of dates may be ripened rapidly after they have reached a certain degree of maturity. Before that time they do not contain sufficient dry matter to make a palatable fruit. Many varieties so ripened are fully equal to the natural product. This may be accomplished by exposing them to the vapors of a great many substances, but only a few are commercially practical, due to the bad flavors which most of them impart. Fruit of good flavor was obtained by treatment with the vapors of acetic and propionic acids, ethyl chloride, ethyl bromide, ethylene chloride, methylene chloride and chloroform, and with solutions of lactic, benzoic and salicylic acids and some other substances of more or less poisonous nature. Gasoline, benzene, esters of organic acids, ordinary ether, acetone, volatile oils and most other substances leave permanent disagreeable flavors.

---

[1] *Compt. rend.*, 149, 58 (1909).

Deglet Noor dates do not yield satisfactorily to these methods but can be made palatable and, if sufficiently mature, will yield fruit of fair quality when subjected to the judicious use of ethyl nitrite vapor. A small amount of this reagent (¼ to ½ cc. of 20 per cent. solution for every 1000 cc. of space enclosed) will finally render the tannin insoluble without discoloring the date badly or imparting any noticeable flavor.

It is anticipated that the application of these methods will prevent much of the enormous loss from souring which is experienced at present during unfavorable weather. Artificially ripened dates do not sour so readily as the fruit ripened on the tree and remain much freer from insects.

ARIZONA AGR EXP STATION,
TUCSON, ARIZONA.

THE ACIDS OF THE PHENYLPROPIOLIC SERIES AND THEIR CONDENSATION TO NAPHTHALENE DERIVATIVES.[1]

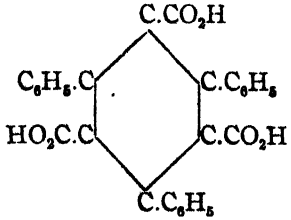
BY JOHN E BUCHER.

Received December 9, 1909

In an investigation of the action of acetic anhydride on acids of the acetylene series in 1895, Michael and Bucher[2] obtained the anhydride of a new acid from phenylpropiolic acid. Three years later,[3] after a thorough study of the compound, they proved it to be the anhydride of 1-phenyl-2,3-naphthalenedicarboxylic acid It was found to have the composition corresponding to the formula $C_{18}H_{10}O_3$ and a molecular weight of 274.

This corresponds to the composition of a phenylpropiolic anhydride $(C_6H_5C \quad C.CO)_2O$, but the acid obtained from it was found to be saturated and entirely different from phenylpropiolic acid. This structural formula evidently does not represent its constitution.

It seemed probable that three molecules of the acid might have polymerized to triphenyltrimesic acid in a manner analogous to the for-



---

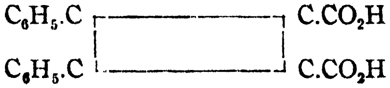
[1] Presented at the Second Decennial Celebration of Clark University, Worcester, Mass., September 14, 1909.

[2] *Ber.*, 28, 2511 (1895).

[3] *Am. Chem. J.*, 20, 89 (1898).

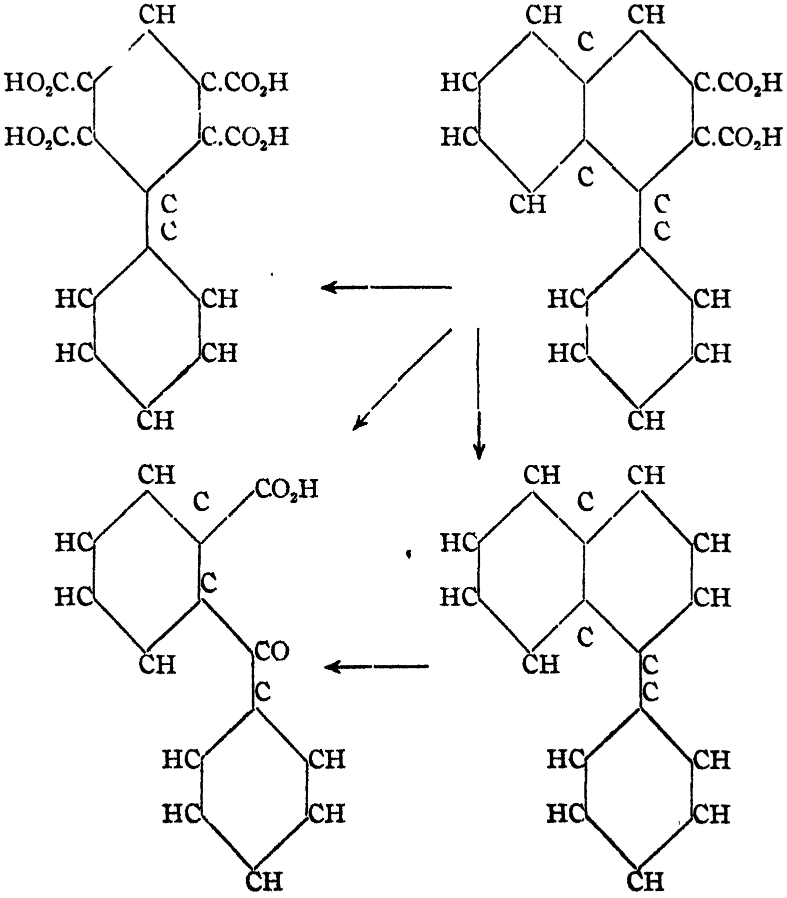
mation of benzene from acetylene. The resulting acid was found to be dibasic and to have only two-thirds of the required molecular weight. These facts showed conclusively that the compound is not the anhydride of triphenyltrimesic acid.

It was then thought possible that the compound might be the anhydride of diphenyltetrenedicarboxylic acid.



This acid would contain two carboxyl groups in the ortho position and it would be dibasic. One might expect benzil among the oxidation products of such an acid but many experiments failed to show the slightest trace of this substance. It was not possible to find any evidence in favor of the tetrene formula.

As none of these three formulas corresponded to the compound, it was evident that the polymerization of the phenylpropiolic acid must have proceeded in a very unusual manner.



They finally succeeded in isolating diphenyltetracarboxylic- and orthobenzoylbenzoic acids from its oxidation products and in preparing its hydrocarbon. The hydrocarbon was also oxidized to orthobenzoylbenzoic acid. The preceding formulas show these transformations.

These facts can only be explained by the above constitutional formula and the compound is therefore the anhydride of 1-phenyl-2,3-naphthalenedicarboxylic acid.

Later, several investigators who evidently had overlooked the above work obtained this compound. Basing their reasoning on insufficient experimental evidence, they described the substance first as the anhydride of triphenyltrimesic acid and afterwards as that of diphenyltetrenedicarboxylic acid, representing structural formulas which had already been shown to be untenable by Michael and Bucher. For example, Lanser[1] obtained the compound by heating phenylpropiolic acid with phosphorus oxychloride, and assigned the formula $C_{54}H_{30}O_9$ for triphenyltrimesic anhydride without making molecular weight determinations.

A little later Manthey[2] determined the molecular weight thus showing the formula to be $C_{18}H_{10}O_3$ and that the constitution must be different from that assigned by Lanser. This evidence together with the fact that the acid contains the two carboxyl groups in the ortho-position, led him to assign the tetrene formula.

In a later paper, Lanser and Halvorsen[3] acknowledge the correctness of Manthey's experimental work and they also accept the tetrene formula. The reactions which they study would, however, apply equally well to other ortho-dibasic acids.

Ruhemann and Meriman[4] also obtained the anhydride in studying the action of phenylpropiolyl chloride on acetone in pyridine solution. They proved the identity of their compound with that of Lanser and regarded it as a terene compound as they did not investigate its constitution.

Michael[5] next showed that the compound described by these investigators is 1-phenyl-2,3-naphthalenedicarboxylic anhydride. He proved this by preparing a specimen by Lanser's method and finding it identical in every respect with a specimen prepared by the method of Michael and Bucher.

Recently, Stobbe[6] obtained this anhydride by the action of light on dibenzalsuccinic anhydride. Failing to get diphenyltetracarboxylic acid by direct oxidation but obtaining ortho-benzoylbenzoic acid, he claimed to have shown the truth of the naphthalene formula of Michael and Bucher for the first time.

These investigators[7] showed that his failure to get the diphenyltetracarboxylic acid was due to incomplete oxidation[8] and that they had noticed the formation of ortho-benzoylbenzoic acid by the *direct* oxidation[1] of the anhydride as well as from the hydrocarbon.

---

[1] *Ber.*, 32, 2478 (1899).

[2] *Ibid.*, 33, 3083 (1900).

[3] *Ibid.*, 35, 1407 (1902).

[4] *J. Chem. Soc.*, 87, 1389 (1905).

[5] *Ber.*, 39, 1908 (1906).

[6] *Ibid.*, 40, 3372 (1907).

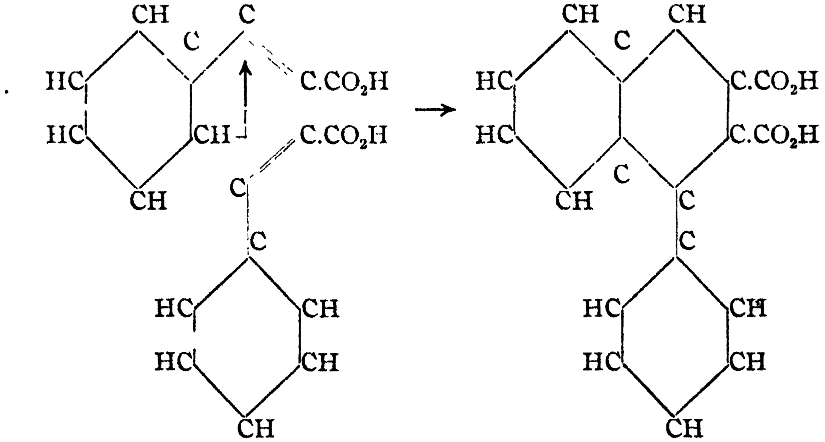
[7] *Ibid.*, 41, 70 (1908).

[8] THIS JOURNAL, 30, 1246 (1908).

Pfeiffer and Möller[2] have polymerized phenylpropiolic ester to the ester of 1-phenyl-2,3-naphthalenedicarboxylic acid by simply heating to 200°. They point out that aromatic acetylene derivatives may thus be polymerized to naphthalene derivatives without the use of condensing agents. The earlier work of Lanser also shows this since Michael has shown that the so-called triphenyltrimesic acid is really a naphthalene derivative. Lanser obtained the anhydride of this acid by heating phenylpropiolic acid to a temperature above 200°. Pfeiffer and Möller's work, however, illustrates the additional fact thatanhydride form ation is not essential for this naphthalene condensation.

I have confirmed Lanser's experiment and have been able to get a much better yield of the ester of the naphthalene acid than Pfeiffer and Moller got. In my experiment, however, the phenylpropiolic ester was polymerized by heating it with acetic anhydride instead of heating it alone.

These investigations show that phenyl propiolic acid and its ester or chloride can be polymerized in a number of different ways to naphthalene derivatives but that the original method of Michael and Bucher which gives a quantitative yield is still the best. The following formulas indicate how this change takes place:



This work has been continued in this laboratory for a number of years in order to determine whether this transformation is general or not. Besides phenylpropiolic acid, eleven of its substitution products have been examined thus far and in every case they polymerized, on heating with acetic anhydride, to derivatives of 1-phenyl-2,3-naphthalenedicarboxylic anhydride. The facts thus far obtained justify the statement[3] that *phenylpropiolic acid and its substitution products show a strong tendency to polymerize, with the wandering of an ortho hydrogen atom, to phenylnaphthalene derivatives.*

---

[1] *Am. Chem. J.*, 20, 112 (1898).

[2] *Ber.*, 40, 3839 (1907).

[3] THIS JOURNAL, 30, 1262 (1908).

In fact, this kind of polymerization is the only form which has been thus far obtained from aromatic propiolic acids.

In this work much time was spent in preparing the aromatic propiolic acids as it was usually necessary to either prepare new compounds or else to improve the methods of preparation of acids which were already known. In most cases methods were found by which these interesting acids could be prepared readily from comparatively inexpensive materials —providing that suitable precautions were observed.

Phenylpropiolic acid was prepared in the usual way from cinnamic acid by making cinnamic ester dibromide. It is well known that alcoholic potash converts this into a mixture of the salts of allo-bromocinnamic acid and bromocinnamic acid and that the latter is easily converted into phenylpropiolic acid by the loss of hydrobromic acid. The former acid is so stable, however, that it is not practicable to convert it into phenylpropiolic acid directly by further heating with alcoholic potash. It can, however, be converted into the isomeric acid by simply heating it. This acid can then be converted, in turn, into phenylpropiolic acid. This change of the labile bromo acids into the corresponding isomeric acids was found to be quantitative in several cases. In the case of the allo-bromocinnamic acid it was noticed that when it was heated with acetic anhydride to 100° its own anhydride was produced but at a higher temperature this was transformed into the bromocinnamic anhydride. The latter could then be transformed into phenylpropiolic acid. From this, it is evident that it is not necessary to use pure phenylpropiolic acid in this work. It generally seemed desirable, however, to separate the acids first. A very good way of doing this is to crystallize them from carbon disulphide or from carbon tetrachloride. In this way it is possible to separate much of the phenylpropiolic acid from the more soluble allo-bromocinnamic acid.

In some other cases, the potassium salts of the propiolic acids were found to be very sparingly soluble in the alcoholic potash, thus yielding the pure acids at once. In all cases the potassium salts of the labile bromocinnamic acids were found quite soluble while the ammonium salts of the isomeric acids were very sparingly soluble. These properties were found very useful in separating the resulting phenylpropiolic acids from these labile substituted bromocinnamic acids which were formed.

The meta- and para-nitrophenylpropiolic acids can be prepared from the corresponding nitrobenzoic aldehydes by Perkin's synthesis. In some other cases Claissen's synthesis was found preferable to that of Perkin.

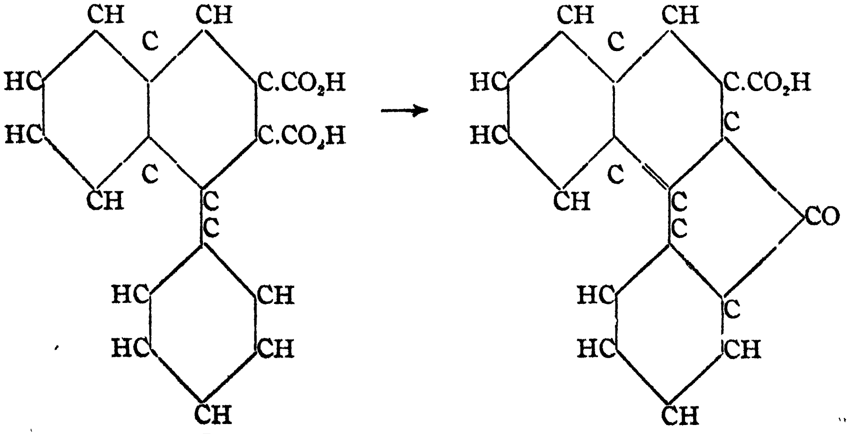
It was also found that the ortho- and para-nitrophenylpropiolic acids could be converted into the corresponding halogen acids by means of the diazo reaction.

Besides phenylpropiolic acid, the following substitution products were prepared: Piperonylpropiolic acid, *o*-chloro-, *o*-bromo-, *m*-nitro-, *m*-chloro-, *p*-nitro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, *p*-methoxy-, and *p*-methylphenylpropiolic acids. These all polymerize readily to derivatives of 1-phenyl-2,3-naphthalenedicarboxylic anhydride when they are heated with acetic anhydride. In the earlier work it was found very difficult to prove this constitution for these products. The method used in case of the first compound has already been described. The meta- and para-nitro compounds were oxidized and then converted into diphenyltetracarboxylic acid thus showing them to be naphthalene derivatives. By means of the diazo reaction, they were then converted into the halogen derivatives identical with those obtained by direct polymerization. This showed the latter to have the same constitution. The constitution of the product from the para-methylphenylpropiolic acid was established by oxidizing it to a diphenylpentacarboxylic acid. In more recent work the very efficient method of oxidizing to benzenepentacarboxylic acid described below was used. By means of this method, which depends on the catalytic action of manganese nitrate in fuming nitric acid, eleven of these acids were oxidized to benzenepentacarboxylic acids, thus confirming the naphthalene constitution which had previously been assigned for some of the substances.

The following description gives an idea of some of the transformations which these substances undergo: They are all ortho-dibasic acids from which water splits out easily on heating. In fact, the first acid obtained is partially converted into its anhydride even on crystallizing it from only moderately heated glacial acetic acid. In this way, I obtained eight grams of the anhydride from twenty grams of the acid. This loss of water in crystallizing the acid from hot solvents led to the statement, made in the first description, that the acid passed into the anhydride spontaneously. This statement was corrected in a later paper by Michael. All of these acids have this general property and some of them, as well as their oxidation products, may show properties similar to those noticed by Orndorff in the case of tetrachlorophthalic acid.

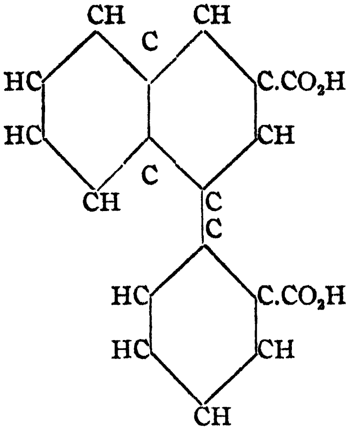
The acids all necessarily contain a carboxyl group with both ortho positions substituted. According to V. Meyer's observations one might expect difficulty in esterifying these acids. This was found to be the case, little or no neutral ester being found, on heating the substances with alcohol and sulphuric acid under the usual conditions. If more sulphuric acid is used and the heating continued for a longer time from 40 to 60 per cent. of neutral ester may be obtained.

Sulphuric acid converts the 1-phenyl-2,3-naphthalenedicarboxylic acid into red allo-chrysoketonecarboxylic acid.



I. II.

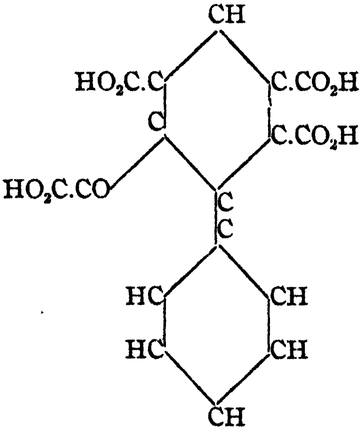
When this red acid is heated to 218° with potassium hydroxide, it is changed practically quantitatively into a new 1-phenylnaphthalenedicarboxylic acid.

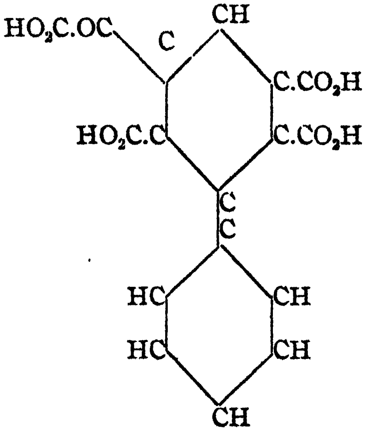


III.

Formulas I, II and III show a method of transferring a carboxyl group from the ortho position on one ring to the corresponding position on the other ring. When the new acid (III) is heated with sulphuric acid, a new red acid different from the allochrysoketonecarboxylic acid (II) is obtained.

The oxidation of these naphthalene acids in alkaline potassium permanganate solution has already been described. The yield of diphenyltetracarboxylic acid is usually small, since the intermediate ketonic acids are very stable towards alkaline potassium permanganate.

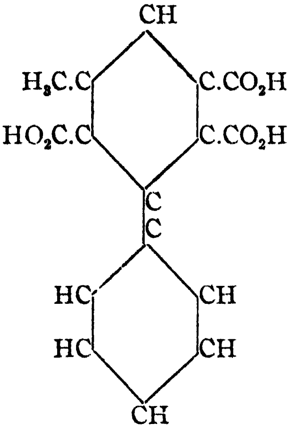




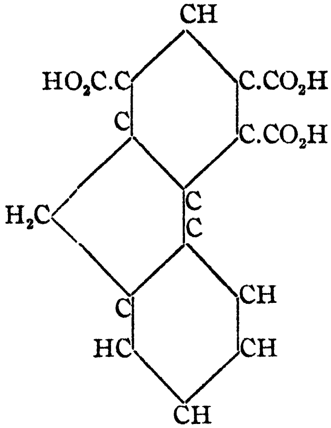
IV. V.

These ketonic acids are very easily oxidized to diphenyltetracarboxylic acids when the solution is acidified. Formulae I, IV, V and VIII indicate these reactions. These acids are obtained in the form of sirup-like solutions and they resemble phthalonic acid closely. Heated with caustic alkalies, they yield diphenyltricarboxylic acids and oxalic acid.

On reduction with hydriodic acid, the *meta*-glyoxylic acid (V) first yields methyldiphenyltricarboxylic acid (VI) which then reduces at a higher temperature to a methylfluorenecarboxylic acid. The isomeric *ortho*-glyoxylic acid (IV), even at the boiling point of hydriodic acid, reduces to a fluorenetricarboxylic acid (VII).



VI.



VII.

This shows the ease with which diphenylcarboxylic acids close the ring to form fluorene derivatives. The same tendency is shown by the action of sulphuric acid on diphenyltetracarboxylic acid (VIII) in forming the yellow diphenyleneketonetricarboxylic acid (IX), which can be reduced to the acid represented by formula VII. I have found this closing of the ring on heating to 100° with sulphuric acid, to take place when all the carboxyl groups were on the same ring but generally not when the carboxyl groups were on different rings. In diphenyleneketonecarboxylic acids of the general form IX, the ring is broken in such a way, on heating with potassium hydroxide, that the carboxyl group is transferred from the ortho position on one ring to the corresponding ortho position on the other.[1] In this case, about 299 parts out of 300 are changed in this way—making the process practically quantitative. The following formulas show these changes.

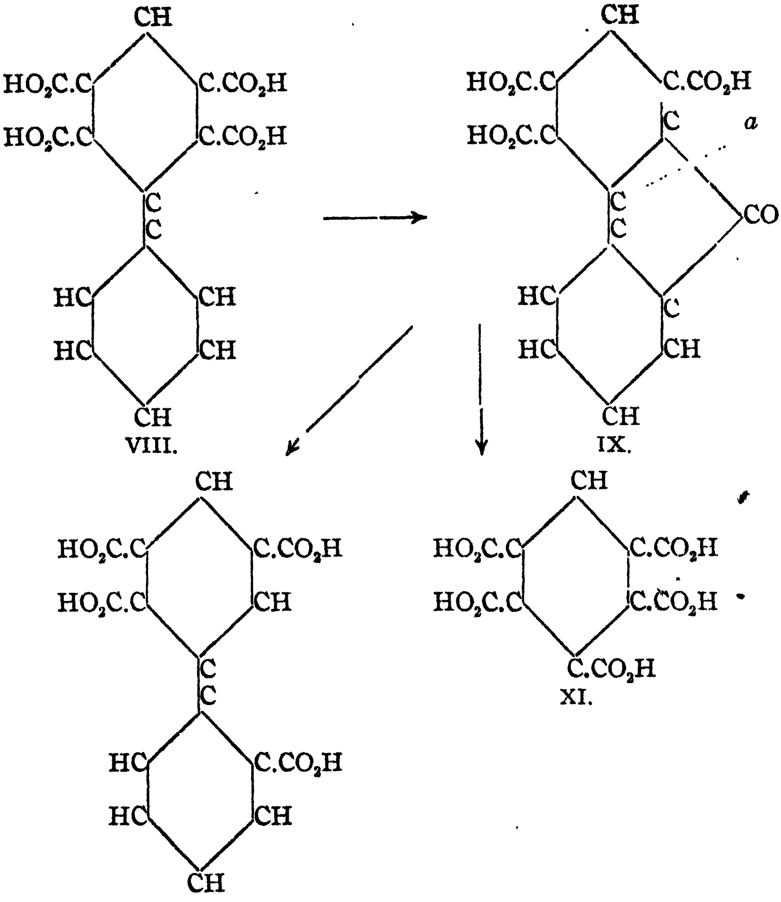
The very sharp breaking of the ring at *a* in formula IX and in the similar case of the red acid (II) indicates a tendency to remove the carboxyl groups as far as possible from each other and suggests the possibility of its giving a means of testing the constitution of the resulting acid. For example Bamberger and Hooker,[2] after heating a yellow diphenyleneketonedicarboxylic acid from retene with caustic alkali, represent the resulting white diphenylenetricarboxylic acid as having the three carboxyl groups on the same ring. This seemed scarcely possible in view of the above facts and an examination showed the acid to have a different structure.

The yellow diphenyleneketonetricarboxylic acid (IX) also furnishes a means of oxidizing these 1-phenyl-2,3-naphthalenedicarboxylic acids or diphenylpolycarboxylic acids (like I and VIII) to benzenepentacar-

---

[1] This Journal, 30, 1261 (1908).

[2] *Ann.*, 229, 159 (1885).



boxylic acids. The latter acid (VIII) is very stable towards alkaline potassium permanganate as on heating for six weeks I recovered 28 per cent. of unchanged acid and could not isolate any benzenepentacarboxylic acid. The yellow acid (IX), however, decolorized the theoretical quantity of permanganate in less than two hours. The very soluble acid product was not completely oxidized but it yielded benzene for the hydrocarbon. Many experiments were made in attempting to complete the reaction but without success. Even heating on the water bath with fuming nitric acid did not aid very much. A small quantity of manganese nitrate was then added to the hot nitric acid. *Brisk effervescence began at once and in a few moments pure benzenepentacarboxylic acid separated from the liquid.* The yield in this experiment was about 90 per cent. of the theory. The manganese nitrate is evidently a very efficient catalytic agent in this case. This method was also applied to the acids without first converting them into ketone derivatives, and, in eleven cases out of the twelve tested, benzenepentacarboxylic acid was found. Not only does this give a very powerful method for determining constitution but it gives a very easy method of preparing the hitherto almost inaccessible benzenepentacarboxylic acid. It also serves for the preparation of other benzene polycarboxylic acids. Bamberger and Hooker's diphenyleneketonedicarboxylic acid from retene can be oxidized in a few hours to two isomeric *benzenetricarboxylic* acids, thus showing that the constitution given for retene and all its derivatives is incorrect.

The above work dealing with the action of acetic anhydride led to the supposition that anhydrides[1] might be prepared from *meta-* and *para*-phthalic acids and their substitution products. On trying the experiment it was found that such anhydrides could be obtained quantitatively by heating a solution of the acid in acetic anhydride to 200° until the excess of reagent was distilled off. These products apparently have a very high molecular weight. A preliminary determination, in nitrobenzene by the boiling point method, for the anhydride from chloroterephthalic acid, $[C_6H_3Cl(CO)_2O]_x$, indicates that it may be as high as 1500 or 2000.

A part of this work has been carried on with the aid of my students and I wish especially to acknowledge the valuable assistance of G. F. Parmenter, N. A. Dubois, V. S. Babasinian, M. L. Dolt, W. C. Slade and F. Keyes.

The more important results of this work thus far are as follows:

1. Satisfactory methods for the preparation of a number of aromatic propiolic acids.
2. The polymerization of these acids to derivatives of 1-phenyl-2,3-naphthalenedicarboxylic acids—giving a quantitative method of synthesis.
3. Syntheses of acids of the diphenyl, fluorene and diphenyleneketone series and a study of their characteristic reactions.
4. Syntheses of benzenepentacarboxylic acid and other benzenepolycarboxylic acids.
5. The determination of the constitution of retene and its derivatives.
6. The preparation of anhydrides from meta- and para-phthalic acids and their substitution products.

BROWN UNIVERSITY, PROVIDENCE, R. I.

CATALYSIS ON THE BASIS OF WORK WITH IMIDO ESTERS.[2]

BY JULIUS STIEGLITZ.

Received December 2, 1909.

I shall not attempt to discuss to-day the general subject of catalysis but shall use the short time rather to present briefly some results[3] in certain lines of our work which seem to shed some light on three fundamental points of interest in catalysis, namely, on the questions how in certain cases a catalytic agent does its work, why it does it, and what limitations there are to its action.

---

[1] THIS JOURNAL, 30, 1263 (1908) and 31, 1319 (1909).

[2] Presented at the Second Decennial Celebration of Clark University, Worcester, Mass., September 15, 1909.

[3] Certain parts of the work are still being carried out—as indicated below—and for such parts this report is preliminary to a final one. Complete discussion of the several parts lay outside the limits of this paper and will be brought in later special reports.

It may be recalled that an imido ester, such as methyl imido benzoate, is very slowly decomposed by pure water. One of the decompositions it undergoes under these conditions is into ammonia and methyl benzoate[1] as expressed in the equation

$$C_6H_5C(: NH)OCH_3 + H_2O \longrightarrow C_6H_5CO_2CH_3 + NH_3. \quad (1)$$

The addition of an acid, say hydrochloric acid, enormously accelerates this otherwise extremely slow action and we were able to show that the acceleration is due to the fact that the reacting component in this decomposition is the positive ion of the ester,[2] as expressed in the equation.

$$C_6H_5(: NH_2{}^+)OCH_3 + H_2O \longrightarrow C_6H_5CO_2CH_3 + NH_4{}^+. \quad (2)$$

In arriving at this conclusion, account had to be taken of the so-called "salt-effect" or "salt-acceleration" produced by the presence of electrolytes, entirely analogous to the "salt-effect" in other decompositions in which water is a reacting component, as in the catalysis of esters by acids. This salt-effect being allowed for, the velocity of decomposition of an imido ester by water in the presence of acids is given in the equation[3]

$$dx/dt = K_{v(ion)} \times C_{pos.\ est.\ ion} \times [C_H \times C_{OH}]. \quad (3)$$

I have not time more than to mention the fact that it was shown that the same fundamental equation may be applied to the saponification of ordinary esters under the influence of acids, the main difference being that for such exceedingly weak oxonium bases as esters are the concentration of the positive ester ion is practically proportional to the concentrations of the ester and the hydrogen ion present at any moment, so that we may transform (3) into[4]

$$dx/dt = K_v \times C_{ester} \times C_H \times [C_H \times C_{OH}] \quad (4)$$

which is also the equation based on experience.

The work on which the above conclusions were based was carried out wholly with the hydrochlorides of the imido esters. More recently we have also carried out measurements with the hydrobromides and nitrates, and begun work also with sulphates; if the positive *ion* is the reacting component, then, determining rigorously the degree of ionization and making rigorous allowance for the salt-effect, we should find that the velocity constant for the decomposition of the positive ion in the chloride solution should also satisfy the observed rates of decomposition of these other salts. For the rigorous treatment, the "salt-effect" produced by the chlorides, bromides, nitrates, etc., has to be determined experimentally and this has been carried out[5] with the chlorides and bromides,[6] mixtures with varying amounts of the potassium and sodium salts being examined, the degrees of ionization of each salt in the mixture being determined with the aid of the principle of isohydric solutions, which was proved to apply to such mixtures.[1] The salt-effect is, except for minute quantities of salt, proportional to its concentration or rather, more probably, only to the concentration of the ionized part of the salt. The salt-effect is an acceleration and if we call $K_{v(ion)o}$ the velocity of decomposition of the imido ester ion in the absence of any salt at all, this velocity will be increased proportionally to some specific acceleration factor A, and to the concentration $m\alpha$ of the ionized part of A salt. So we have

---

[1] Stieglitz, *Report International Congress of Arts and Science*, St. Louis, 4, 276 (1904), and *Am. Chem. J.*, 39, 29 (1908).

[2] Stieglitz with Derby, McCracken, Schlesinger, *Am. Chem. J.*, 39, 29, 166, 402, 437, 586, 719.

[3] $C_{pos.\ est.\ ion}$ is a function of x.

[4] C_{ester} is a function of x.

[5] W. W. Hickman, Dissertation, 1909.

[6] Mr. Weatherby is completing the work begun by Mr. Hickman on the nitrates and sulphates.

$$K_{v(ion)obs.} = K_{v(ion)o}\,(1 + A\,m\,\alpha). \qquad (5)$$

$K_{v(ion)obs.}$ is the constant calculated according to equation (3) from the observations without any allowance for a salt-effect.

$K_{v(ion)o}$, the velocity constant when the salt effect is eliminated, is easily found by extrapolation from the observations when imido ester salts are present without added salts, A from the results obtained when salts have been added. We arrived thus empirically at the rather unexpected result that the accelerating factor A is approximately the same for sodium, potassium and lithium chlorides and for the bromides as well as for the chlorides, *viz.*, about 185 per cent. per gram molecule of fully ionized salt. Table I illustrates this fact for potassium chloride and potassium bromide. K_v is the velocity coefficient calculated without regard to the degree of ionization of the imido ester salt, α is the degree of ionization of the salt calculated with the aid of the principle of isohydric solutions. In the columns headed "found" are given the values obtained for K_v/α by experiment; in the columns headed "calculated" are the values obtained according to equation (5), in which the velocity coefficient $K_{v(ion)o}$ in the absence of any salts at all is taken as 164 and the salt acceleration factor A is taken as 185 per cent. for both series.

TABLE I.[2]

K Hal.	KCl. 43430 K_v/α.		KBr. 43430K_v/α.	
m.	Found.	Calculated.	Found.	Calculated.
0	176	176	176	177
0.1	191	190	191	190
0.2	213	214	209	215
0.25	227	226	230	227
0.333	247	245	(268)	247

I wish to emphasize this result because the work of others, notably of Arrhenius and Euler, with cane-sugar and esters, shows varying specific accelerating factors for these salts. I believe our work has the advantage of our knowing from conductivity measurements the degrees of ionization of the imido ester salts as well as of the added electrolyte so that there seems to be no unknown factor left in our estimations. But we are simply presenting these results for the time being as an empirical contribution to the whole question of catalysis and we do not consider the very complex question of "salt catalysis" as at all settled.[3]

---

[1] Edith E. Barnard, Dissertation, 1907.

[2] Taken from W. W. Hickman's dissertation.

[3] Work on "salt catalysis" is being continued by L. S. Weatherby, preliminary results by Mr. Hickman on the effect of sulphates indicated an abnormally high effect.

With the aid of the determination of the salt factor for chlorides and bromides we have been able to show that the positive ester ion shows indeed the same rate of decomposition irrespective of its origin from either of these salts and very probably also for the nitrate[1] (see the values for $K_{v/\alpha}$ for the three salts in equi-molar concentrations as given in Table II). This is exactly what our theory would require, namely, that the simple reason why the addition of an acid accelerates this decomposition is that it forms a salt whose positive ion is the reacting component and that the concentration of the ion is enormously increased when the catalyzing acid is added to the free ester, which is a very weak and therefore little ionized base.

TABLE II.[2]—ETHYL IMIDO BENZOATE.

	Hydrochloride.			Hydrobromide.			Nitrate.		
m.	α.[3]	Kv.[4]	Kv/α.	α.[2]	Kv.[2]	Kv/α.	α.[2]	Kv.[2]	Kv/α.
0.05	77.8	136	175	75.9	133	176	75.1	133	177
0.1	71.8	132	185	69.4	128	184	68.3	127	186
0.2	64.5	121	188	61.7	119	193	60.4	118	195
0.33	57.7	114	198	54.7	108	198	52.7	107	201

It was suggested by Arrhenius and emphasized by Euler that the salt acceleration is probably largely due to the increased ionization of water in the presence of electrolytes, but quantitative evidence in support of such a conclusion has not been brought, as far as I am aware. In view of the increase observed by Arrhenius and others[5] in the strength of other acids in the presence of added foreign salts, *e. g.*, of acetic, formic and carbonic acids in the presence of sodium chloride, it seems a sufficiently rational assumption that water should show a similar increased ionization.[6] The imido esters, enabling us to measure the actual concentration of the reacting imido ester ion, gave us an opportunity to bring experimental evidence strongly supporting this view. From equation (3) it is obvious that if the salt acceleration is due to the increased ionization of water, *viz.*, an increase in the value of the third factor, $(C_H \times C_{OH})$ then, $C_{pos.\ est\ ion}$ being known by experiment, the velocity constant $K_{v(ion)}$ calculated *without* taking any increased value of $[C_H \times C_{OH}]$ into account, should increase in the same proportion for all the imido esters for the same concentration of added salt ions, irrespective of the fact that, according to the ester used, the decomposition may be a comparatively slow or a very fast one. We have found this to be true[7]—all the esters used show the same acceleration per gram molecule ionized salt—*i. e.*, close to 185 per cent. per gram molecule ionized potassium chloride, etc.[8]

Having found that the reacting component in these and a number of other actions under the influence of acids is the positive ion of a salt formed with the acid, we were naturally most interested in the question

---

[1] The salt effect for nitrates is now being determined.

[2] Taken from W. W. Hickman's dissertation.

[3] Taken from Edith E. Barnard's dissertation.

[4] Taken from Schlesinger's results, *Loc. cit.*

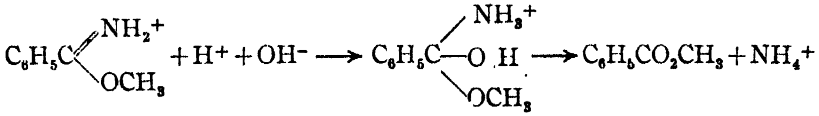
[5] E. J. Szyszkowski, *Z. physik. Chem.*, 58, 419.

[6] See a discussion of the other side of this question by Acree, *Am. Chem. J.*, 41, 474.

[7] Dissertation of Edith E. Barnard and W. W. Hickman.

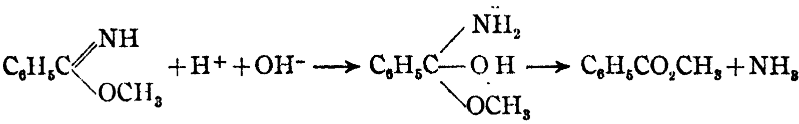
[8] The investigation of the ionization of water in salt solutions is being continued with other substances and by other methods.

why the *ion* should be so reactive, why it should be so important a component. We can hardly consider the decompositions to be *purely* ionic reactions,[1] comparable with the hydrolysis of salts in aqueous solutions, as was mistakenly assumed, for instance, by Euler and by Kastle. Such assumptions run counter to the law of mass action applied rigorously in the analysis of the conditions.[1] The law is, however, in agreement with the assumption[2] based on experience gained in organic chemistry that the following are the stages for the action:



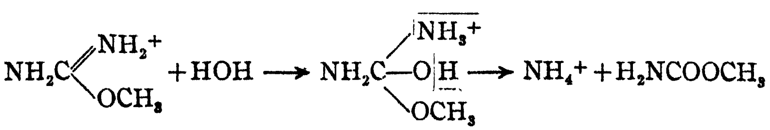
$$C_6H_5C\begin{smallmatrix}\diagup NH_2^+\\ \diagdown OCH_3\end{smallmatrix} + H^+ + OH^- \longrightarrow C_6H_5C\begin{smallmatrix}\diagup NH_3^+\\ -O\,H\\ \diagdown OCH_3\end{smallmatrix} \longrightarrow C_6H_5CO_2CH_3 + NH_4^+ \qquad (6)$$

Now, we may well ask why this should be an enormously faster action than the entirely analogous possible action of water on the non-ionized free ester, which, it is clear, could proceed in a very similar series of stages as expressed in the equations:



$$C_6H_5C\begin{smallmatrix}\diagup NH\\ \diagdown OCH_3\end{smallmatrix} + H^+ + OH^- \longrightarrow C_6H_5C\begin{smallmatrix}\diagup \ddot{N}H_2\\ -O\,H\\ \diagdown OCH_3\end{smallmatrix} \longrightarrow C_6H_5CO_2CH_3 + NH_3. \qquad (6')$$

For me, one of the most interesting and important features of our work is found in the unmistakable way in which the fact is brought out more and more clearly that the accelerating or catalytic effect of the acid is most intimately associated with the transformation, in acid solution, of the positive ion of a weaker base into that of a stronger one—the results no doubt of the principle of the loss of a maximum amount of free energy.[3] This is shown most strikingly in the following illustration: whereas the above imido esters are very rapidly decomposed by water in the presence of acid, this is not the case for the closely related compounds, the urea ester salts, which, *structurally considered*, could react quite as easily with water but are as a matter of fact quite stable in acid solution. The transformation



$$NH_2C\begin{smallmatrix}\diagup NH_2^+\\ \diagdown OCH_3\end{smallmatrix} + HOH \longrightarrow NH_2C\begin{smallmatrix}\diagup \overline{NH_3^+}\\ -O|H\\ \diagdown OCH_3\end{smallmatrix} \longrightarrow NH_4^+ + H_2NCOOCH_3 \qquad (7)$$

only takes place to a very slight extent at 100°, and at ordinary temperatures, where imido ester salts are completely decomposed in one to ten hours, the urea ester salts have not been observed to decompose at all.[4] In this case we have the notable fact that such a transformation would involve the change of a salt of a stronger base into that of a much weaker one—an ammonium salt—and this does not take place. To test the legitimacy of our reasoning we recently examined the behavior of benzoyl urea ester salts: the benzoyl urea esters form very much weaker bases than ammonia and our reasoning would lead us to expect that they, in turn, ought to be decomposed quite as smoothly in acid solution as the imido esters. Such is, in fact, the case;[1] urethanes and ammonium salts readily result according to the equation

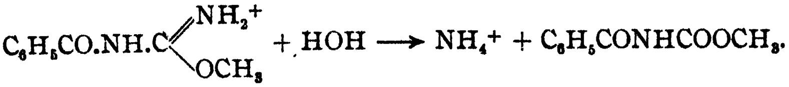
---

[1] See a more complete discussion by Stieglitz, *Am. Chem. J.*, 39, 402.

[2] Stieglitz, *Loc. cit.*

[3] *Ibid.*

[4] The degree of stability is being examined *quantitatively*.



$$C_6H_5CO.NH.C\begin{matrix}\diagup NH_2^+\\ \diagdown OCH_3\end{matrix} + HOH \longrightarrow NH_4^+ + C_6H_5CONHCOOCH_3. \quad (8)$$

We find then that perfect analogy in structure is of far less importance in determining the result of the action of water than a definite physico-chemical relation subject to quantitative measurement.

This is again brought out beautifully by the behavior of the urea esters towards ammonia. The imido esters give with ammonia amidines and again the action is accelerated by the addition of an acid or an ammonium salt and, as we shall see presently, this is due to the fact that again it is the positive ester ion that reacts with ammonia, an amidine resulting according to the equation

$$C_6H_5C(: NH_2^+)OCH_3 + NH_3 \longrightarrow C_6H_5C(: NH_2^+)NH_2 + HOCH_3 \quad (9).$$

Now, urea esters which, as explained above, would not react with *water* in acid solution because the salt of a stronger base would be converted into the salt of a weaker one if they did react, would give with *ammonia* guanidines which are still stronger bases than they are themselves. They should, therefore, according to this theory, react with ammonia in the presence of an acid; as a matter of fact they do, producing guanidines very readily, and we were able to prove again that the velocity of the formation is proportional to the concentration of the positive ester ion;[1] in fact, until our theory led us to recognize the importance of having a salt-forming acid present, all our efforts to prepare guanidines from urea esters—by using ammonia alone—had proved futile; so that this theory seems to agree equally well with the reactions of a given compound which *do occur* as with those which do not take place.

We have found too that in series of structurally closely related esters where what might be called the structural and stereochemical resistances to the action are perhaps approximately the same, the transformation of the positive ion of a weaker base in the presence of acids into that of a given stronger base, say into the ammonium ion, *proceeds with the greater velocity at a given temperature the weaker the original base is.*[3] This brings, as far as I am aware, the first complete experimental proof of a theory which others, notably van't Hoff and Euler suspected to be true,[4] although there appeared so many marked contradictions to the assumption that the theory appeared at best a very uncertain one. For instance, Hemptinne[5] and Lowenherz,[6] working on this problem at van't Hoff's suggestion, obtained the following results for the saponification of esters by acids:

---

[1] J. C. Moore's dissertation, 1909.

[2] R. A. Hall's dissertation (1907).

[3] Cf. Stieglitz, *Loc. cit.*, and McCracken, *Loc. cit.*

[4] See the discussion by Euler, *Z. physik. Chem.*, 36, 410.

[5] *Ibid.*, 13, 561.

[6] *Ibid.*, 15, 395.

TABLE III.[1]

Ester.	Velocity constant.	Ioniz. const. of the acid.
$HCOOC_2H_5$	0.11	$21 \times 10^{-}$
$CH_3COOC_2H_5$	0.0057	1.8×10^{-5}
$ClCH_2COOC_2H_5$	0 0033	$155 \times 10^{-}$
$Cl_2CHCOOC_2H_5$	0.0053	$5100 \times 10^{-}$
$CH_3CH_2COOC_2H_5$	0 0061	$1.3 \times 10^{-}$

Assuming, as Euler did, that the strongest acids produce the weakest bases in their esters, one might expect the positive ions of the chloroacetic acid esters to be saponified most rapidly to give the positive ion of a *given* stronger base, the oxonium base of ethyl alcohol. As a matter of fact the velocity constants in the above table do not tell us anything at all as to whether that is so or not and that is why the theory, heretofore, has appeared as an unproved one; obviously it does not follow from the data in Table III, where the *weakest* bases, dichloroacetic ester and chloroacetic ester, have the *smallest*, not the largest, velocity constants of decomposition. But the fact that, for instance, the velocity coefficient for the saponification of dichloroacetic ester is even smaller than that for ethyl acetate *does not mean anything at all* in regard to the real *relative rates of transformation of their positive ions*: there is a second factor involved, namely, the concentrations of the positive ions of the esters are dependent on the strength of the esters as oxonium bases, as expressed in our fundamental equations for the catalysis of an ester by an acid.[2] In our fundamental equation

$$dx/dt = K_{v(ion)} \times C_{pos.\ est.\ ion} \times [C_H \times C_{OH}] \qquad (10)^3$$

we may substitute for $C_{pos.\ est.\ ion}$ the relation expressed in:

$$C_{pos.\ est.\ ion} = k_{aff.}/k' \times C_{ester} \times C_H \qquad (11)^4$$

and have

$$dx/dt = K_{v(ion)} \times k_{aff.}/k' \times C_{ester} \times C_H \times [C_H \times C_{OH}] \qquad (12)$$

$$= K_v \times C_{ester} \times C_H \times C_H \times C_{OH} \qquad (13)$$

which is the ordinary equation representing the velocity of decomposition of esters by acids. What we determine with esters, for instance in Hemptinne's and Lowenherz's work as expressed in Table III is K_v and not the *more fundamental constant* $K_{v(ion)}$. Now

$$K_v = K_{v(ion)} \times k_{aff.}/k' \qquad (14)$$

and it is obvious that if the basic strength of the ester as expressed in $k_{aff.}$ grows very much smaller, as it undoubtedly does when we go from ethyl acetate to ethyl chloroacetate, $K_{v(ion)}$ *could easily grow very much larger* and *yet* K_v *need not change appreciably or it might even grow smaller*, without the result being in any disagreement whatever with the theory expressed. This means, of course, that determinations simply of the velocity constants K_v of decomposition of such esters do not prove anything as to the principle at issue. A somewhat stronger base might well give a higher rate of change than a weaker one by virtue of the fact that a larger proportion of the base is present in its active form, the ion, and the real rate of decomposition of the ion may be much smaller than that of an ester giving a smaller velocity constant K_v. The imido esters have the advantage that their affinity constants are easily ascertained and we do not deal with any such unknown quantity at all, and thus we were able to bring what I believe is the first experimental proof of the soundness of the theory. An apt illustration of the correctness of our argument concerning the lack of data for a correct analysis of results like those given in Table III is found in the following facts: the formation of amidines from imido esters, as was stated, is greatly accelerated by the addition of acids or of an ammonium salt and we were able to show that the amidine formation may be considered essentially a function of the concentration of the positive ester ion, proceeding according to

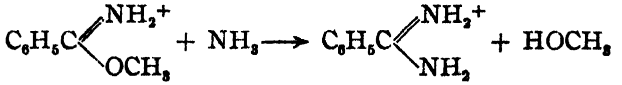
---

[1] The table is taken from Euler, *Loc. cit.*, p. 412.

[2] Stieglitz, *International Congress of Arts and Science*, St. Louis, 1904, **4**, 276 of the report, and *Am. Chem. J.*, **39**, 47 (1908).

[3] $C_{pos.\ est.\ ion}$ is a function of x.

[4] k' is the stability constant of the oxonium hydroxide. $k_{aff.}/k'$ may be considered the stability constant of the complex ester ion. Cf. Bredig, *Z. Elektrochem.*, **9**, 118 (foot-note).


$$C_6H_5C{\Large\langle}^{NH_2^+}_{OCH_3} + NH_3 \longrightarrow C_6H_5C{\Large\langle}^{NH_2^+}_{NH_2} + HOCH_3 \qquad (9)$$

and

$$dx/dt = K_v \times C_{pos.\,est.\,ion} \times C_{NH_3} \qquad (15)^1$$

Now, if we develop the expression for the concentration of the positive ion of a very weak base like an imido ester in the presence of a much stronger one like ammonium hydroxide we find that:

$$C_{pos.\,est.\,ion} = \frac{C_{ester} \times C_{NH_4^+}}{C_{NH_3}} \times \frac{k_{aff.\,est.}}{k_{aff.\,amm.}} \qquad (16)$$

and by substitution we get:

$$dx/dt = K_{v(ion)} \times \frac{k_{aff.\,est.}}{k_{aff.\,amm.}} \times \frac{C_{ester} \times C_{NH_4^+}}{C_{NH_3}} \times C_{NH_3} \qquad (17)$$

$$= K_{v(ion)} \times \frac{k_{aff.\,est.}}{k_{aff.\,amm.}} \times C_{ester} \times C_{NH_4^+}. \qquad (18)^2$$

Now, imido *ethyl* benzoate forms benzamidine considerably faster than does the *methyl* ester: in both cases the change is from the salt of the positive ion of a weaker base to that of a much stronger one, the amidine, but the *ethyl* ester is the stronger base and yet it reacts the faster and apparently contradicts our theory. A knowledge of the affinity constants shows, however, that it reacts the faster only because by virtue of its being a stronger base it takes a larger proportion of the catalytic agent, the acid, from the ammonium chloride, and forms a proportionally larger concentration of the active component, the ester ion, than does the methyl ester under the same conditions. Calculating with the aid

---

[1] $C_{pos.\,est.\,ion}$ is a function of x.

[2] In passing, it may be remarked that this last form shows that the action may be considered one of the ion ammonium acting on the ester, but we believe our original assumption to be the right one for reasons found in the behavior of organic compounds which cannot be elaborated here; it may be said, for instance, that we have found NH_3 and not NH_4^+ to react with ordinary esters to form amides and are carrying out other more crucial experiments on this point. *Vide* Acree, *Am. Chem. J.*, 38, 308. itzgerald and Lapworth, *J. Chem. Soc.*, 93, 2163.

of the affinity constants the true *velocities of transformation of the positive ions*, we find the true relation: $K_{v(ion)}$ for the methyl ester is 140/0.434 and for the ethyl ester only 69/0.434.[1] So the true relations resulting from an exact knowledge of all the quantitative constants involved agree perfectly with the fundamental principle given.

This reaction shows other points of great interest: for instance, the fact that the concentration of ammonia cancels out of the mathematical equation leads to the conclusion that the velocity of decomposition is independent of the concentration of ammonia, one of the reacting components.

This peculiar conclusion has been fully verified by experience; the velocity constant is as a matter of experiment almost, although not absolutely, independent of the concentration of ammonia; in the case of the above methyl ester, the constant grows only about 10 per cent. with an increase of 400 per cent. in the concentration of the ammonia. This apparent contradiction with the law of mass action is readily understood if we remember that the concentration of ammonia has two effects which oppose each other; ammonia does accelerate the action in proportion to its mass as required by the law, but it also to the same degree retards the action by depriving the weaker base of the ionizing and therefore catalyzing acid. Within a year Lapworth[2] has made the extremely important discovery that water stands in exactly the same relation to the esters in the catalysis by acids—only then the two bases competing for the acid are two oxonium bases, the ester and water.

And now in conclusion I wish to call attention to one more result with these imido esters which has impressed us very much and which seems to me to throw a very clear light on the whole question of catalysis or acceleration by showing certain limitations to catalytic effects. It was mentioned a moment ago that the velocity of formation of benzamidine from methyl imido benzoate may be expressed as a function of the positive imido ester ion and that it is almost independent of the concentration of the ammonia; but it is not absolutely independent, there is a slight but steady rise in the value of the constants with increasing concentrations of ammonia. All other secondary reactions having been excluded (*e. g.*, for fourfold increase of NH_3, the constants rise gradually from 139/0.434 to 154/0.434) as the cause of this increase by a knowledge of their velocity constants, we suspected that besides the main action of ammonia on the positive ester ion, there is a much slower action of ammonia also on the non-ionized free ester, namely, that we have two simultaneous actions:

$$C_6H_5C(:NH_2^+)OCH_3 + NH_3 \longrightarrow C_6H_5C(:NH_2^+)NH_2 + HOCH_3 \quad (18)$$

and

$$C_6H_5C(:NH)OCH_3 + NH_3 \longrightarrow C_6H_5C(:NH)NH_2 + HOCH_3 \quad (19)$$

We had the more reason to suspect this as we had already found that water, besides decomposing the positive ion of an imido ester at a very high speed, also undoubtedly decomposes the non-ionized ester at a very slow rate.[3] It was found that the experimental results agree very well with this conception of two simultaneous actions in the formation of

[1] Miss Katharine Blunt's dissertation (1907).

[2] *Loc. cit.*

[3] In this case the products are different. *Vide* Stieglitz, Derby and Schlesinger, *Loc. cit.*

benzamidine and that the velocity constant for the action of ammonia on the positive ester methyl ion at 25° is 325, while that on the ester molecule is only 0.0069.[1] That is, the positive ion is almost 50,000 times as reactive as the non-ionized molecule. It may appear somewhat surprising that such a small constant could still be detected side by side with such an enormous one, the whole action being completed in one to two hours. But we must remember that for the ion action with the enormously high rate of change we have at any moment only minute quantities of the reacting component, *e. g.*, 0.000,005 gram ion at the beginning of a velocity measurement, which is used up at an enormous speed but always formed again instantly by the purely ionic action of imido ester on the ammonium chloride. On the other hand the transformation of the non-ionized molecule has the advantage of relatively high concentrations of each of the reacting components, say 0.05 both for the ammonia and for the free ester at the beginning of an action. With a concentration many thousand times in its favor it is then not surprising to find this very slow action becoming perceptible in careful quantitative work. Now, if we should use a much weaker base still, we might easily find the action with the non-ionized ester taking a *more and more prominent part* in the total change, even if the actual rate of change of the positive ester ion should still be very much the greater. We have recently found such to be the case for the action of ammonia and ammonium chloride on benzoyl urea ester:[2] the velocity constants are so nicely balanced against the affinity constants that the observed changes did not agree even approximately with either conception used alone, *viz.*, that the guanidine formation was due to the action of ammonia on the positive ester ion alone, or on the non-ionized ester alone. But they did agree well with the view that both actions occur simultaneously, the velocity coefficient for the action on the ion being 34.5 and the coefficient for the action on the non-ionized ester being 0.0015, a ratio of 23000 to 1 again. We were exceedingly pleased to find this case because it forms the connecting link with what we have found to be true for the formation of ordinary acid amides from acid esters in the presence of ammonia and ammonium salts:

$$CH_3COOCH_3 + NH_3 \longrightarrow CH_3CONH_2 + HOCH_3 \qquad (20).$$

This action seems to be essentially a function of the ester and ammonia and it is an extremely slow reaction.[3] We can easily understand this case now; the esters as extremely weak oxonium bases must be able to take only the faintest traces of acid from the ammonium chloride in the presence of ammonia and therefore the slow molecular transformation comes to the front as enormously favored by the concentrations of the reacting components. In the case of the actions of acids on esters and water, the esters compete only with an oxonium base of the same order of strength as they are themselves and rather weaker,[4] the oxonium base of water and here the reaction with the ion is again predominant.

These studies then show us a whole range of organic compounds, obviously of the *same type* and *family* but giving reactions which proceed quite differently with the imido esters the action of ammonia on the *positive ion* is the essential action and the use of a catalytic agent,[1] an acid is advisable, in fact, necessary; with ordinary esters the action on the ion becomes negligible because the ion simply cannot be produced in sufficient quantity under these conditions and the action *of ammonia on the non-ionized ester becomes the essential action.* The addition of acid as a catalytic agent is *practically ineffective* and therefore inadvisable. But these apparently disconnected results are now easily understood as being perfectly consistent and logical—the one case representing an almost but not quite pure type of one of the *two natural simultaneous reactions*—the enormously rapid action of the ammonia on the *imido ester ion*—and the other case representing the almost pure type of the other simultaneous action, the extremely slow action of ammonia on the non-ionized ester molecule. And the connecting link is found when the adjustment of the affinity and the velocity constants involved bring *both actions out prominently at the same time.* Of course one must then expect every possible class of reactions lying between these extremes. The results show plainly then, I believe, why a catalytic agent will work smoothly in a number of cases, and why it will fail utterly in accelerating actions apparently of exactly the same organic type, *differing only in the numerical value of the physico-chemical constants included in the final expression governing the action of a catalytic agent.* We have been using the imido esters *simply as a kind of magnifying glass* to *measure* all these constants and thus to enable us to recognize some of the general underlying principles which govern catalysis by such chemical agents, as acids, bases and salts.

---

[1] Mr. Norton is collecting more data on these relations.

[2] J. C. Moore's dissertation (1909).

[3] Unpublished work by J. Stieglitz and Dr. Barnard.

[4] Lapworth, *Loc. cit.*

ON THE BIOCHEMISTRY OF NUCLEIC ACIDS.[2]

BY P. A. LEVENE.

Received December 2, 1909

Life is the most complex phenomenon in nature and its manifestations are innumerable. They all mysteriously arise in the living organism and are all harmoniously centered in it. This, even in its simplest form is the most perfect laboratory, the seat of an infinite number of chemical reactions, none of them interfering with the equilibrium of the others. The substances produced by the most primitive of the living organisms are as large in number as they are varied in their properties. The discoveries of new substances manufactured by the plant or animal cell are not yet exhausted and for ages the chemist dreamed of no better reward for his labors than the finding in tissue juices of a new body with properties hitherto unknown. The living organism was the only retort, vital force the only reaction in his possession that could furnish him with carbon-containing substances. In that sense every chemist in those days was a biological chemist.

In the year 1828 a startling discovery was announced. Wöhler wrote to Berzelius: "I must tell you that I can make urea without the aid of the kidney, or generally without the living organism whether of man or dog," and four years later the divorce of biological and organic chemistry was apparently accomplished when Wöhler and Liebig laid the foundation of the organic chemistry of to-day by their work on the radicle of benzoic acid. However, the divorce was only apparent, for the reason that only the knowledge of molecular constitution made it possible to establish the relationship between the organism and the chemical bodies manufactured by it, only the knowledge of the dynamics of the chemical reactions could coördinate the observations of the functions of the living organism, and of the accompanying changes in the composition of the living cells.

---

[1] *Loc. cit.*

[2] Presented at the Second Decennial Celebration of Clark University, Worcester, Mass., September 15, 1909.

The attitude of the biological chemist was altered. He saw his new goal in disclosing the nature of chemical reactions occurring within the living cell and finding their bearing on the manifestations of life.

If time permitted I would present to you the progress of all the work done in that direction in recent years. Within the narrow limits of this report, however, this is impossible to accomplish with any degree of justice to the subject and I shall, therefore, limit the discussion to only one phase, namely, to the work bearing on the chemical interpretation of one of the most cardinal properties of living matter.

Living matter is distinguished from inanimate by the fact that it undergoes cleavage and oxidation at a very perceptible velocity, and that the restoration of the loss sustained in that manner takes place at approximately the same rate. Thus the function of automatic regeneration lends to living matter its principal peculiarity.

Great credit is due to the biologist for the discovery that in an organized cell this function is seated in a formation possessing definite chemical properties, named chromatin or nuclein. At a time when the process of regeneration is very active, namely, during the development of the fertilized egg, the rate of the new formation of nuclein rises to a very perceptible degree, and the observer is led to see a genetic relationship between these two processes.

Our distinguished biologist, Jacques Loeb,[1] was the first to express the function of reproduction in terms of chemical reactions. In his address to the International Congress of Zoologists held in Boston in September, 1907, he stated: "If the question be raised as to what is the most obvious chemical reaction which the spermatozoan causes in the egg, the answer must be an enormous synthesis of chromatin or nuclear material from constituents of the cytoplasm." Thus, it becomes evident that the knowledge of the mechanism of regeneration is dependent on the knowledge of the chemistry of nucleins.

I shall for a moment forestall the systematic discussion of the chemical nature of nucleins by mentioning that at the time of Loeb's address we were in possession of considerable information on the composition of these substances. It was known that phosphoric acid entered into the formation of the molecule. Therefore, it became evident to Loeb that a supply of phosphoric acid was required in order to make a synthesis of nucleins possible. In a developing egg the phosphoric acid was furnished by the cell itself, for the formation of nucleins proceeded also when the eggs were placed in a medium free of phosphoric acid. The other components of the cell that are known to contain phosphoric acid in their molecule are the lipoids. In these substances phosphoric acid

---

[1] University of California Publications in Physiology, 3, 61–81 (1907).

is present in an ester-form combination, and Professor Loeb proceeded to argue that the first phase in cell reproduction *à priori* ought to consist in the saponification of its lipoids. This assumption was brilliantly verified in his experiments on artificial parthogenesis. He brought to light the fact that dissolution of the lipoids is actually the process which precedes the nuclein synthesis and the segmentation of the nucleus. He further demonstrated that agencies facilitating this saponification were able under favorable conditions to start the development of an unfertilized egg without the aid of spermatozoa. Thus only an elementary knowledge of the chemical nature of two cell components furnished Professor Loeb with the power at will to start or to impede cell development by chemical means, and in a way to furnish evidence that the function of regeneration was a chemical process. But the process of nuclein synthesis in the active cells is not yet disclosed in its harmonious entirety, and no one can entertain any hope of arriving at this knowledge without the discovery of the chemical constitution of nucleins.

The considerations that attracted the attention of so many chemists to the work on the chemical nature of these substances, therefore, are becoming very obvious, and I shall attempt to present the results and the achievements of the numerous endeavors towards the solution of this very difficult problem.

The first important contribution to the chemistry of nucleins was made by Altman, a biologist.[1] Altman was in possession of the information that nucleins were endowed with the properties of fairly strong acids, and further that they were quite resistant to the action of pepsin hydrochloric acid. The latter property enabled him to prepare considerable quantities of nuclein by removing the protein part of the tissues by means of peptic digestion, and the fats by the usual extractives. The remaining nuclein he found to consist of a protein combined with a conjugated phosphoric acid. The acid he named "nucleic acid." By means of alkaline hydrolysis, Altman succeeded in removing all the protein from his nuclein so that the final product analyzed by him refused to disclose any trace of protein even by the aid of the most sensitive color test.

The further development of the chemistry of nucleic acid was accomplished through the investigations of Miescher, of Schmiedeberg and his pupils, of Kossel and his school, by Haiser, G. H. Hammarsten and his pupil Ivar Bang, and in this country by the work of T. B. Osborne, of Walter Jones, and of my co-workers and myself. I must, however, add that the purest nucleic acid was obtained by the man who was first in so many lines of chemical activity, Liebig, although on this occasion he failed to discover the real significance of his finding.

I shall make no attempt to present all the work on nucleic acid in its chronological order, but I shall refer to individual investigations in connection with the discussion of the development of the various phases in our knowledge of chemical structure of those complex acids.

The three principal phases in the endeavors to reveal the nature of nucleic acid consist: first, of work aiming to obtain the substance in a convenient manner, and in a possibly unaltered condition with a view to ascertain the elementary composition of the substance; second, in the work directed towards finding all the components of the various nucleic acids; and third, in determining the actual structure of the molecule; or in other words the manner of arrangement of the individual components within the molecule.

---

[1] *Arch. Anat. und Physiol. Physiol. Abt.*, 1889, 524.

Ultimate Analysis of Nucleic Acids.

I shall touch only briefly on the first phase of the work, for the reason that it is of interest principally to the men personally engaged in it. The achievements obtained through that work are not very significant. Only in connection with the study of inosinic acid, a nucleic acid of beef muscle, the elementary analysis was of unmistakable service in ascertaining the composition of the substance. It was the first and thus far the only instance that a salt of a nucleic acid was obtained in a crystalline form. The fact that no other nucleic acid has been prepared in an absolutely pure condition renders the conclusions drawn from their analysis only of secondary value. The workers who contributed to the improvement in the methods of preparation of the substance are: Altman, Miescher, Schmiedeberg, Kossel, Neumann, Hammarsten, Bang, Haiser and myself.[1]

The methods of preparation and of purification of the substance employed by individual workers differed greatly either in principle or detail. Under such circumstances marked divergence was noted in the analytical figures obtained by different investigators for nucleic acids even of the same origin. The following table illustrates some of these discrepancies.

TABLE SHOWING THE ELEMENTARY COMPOSITION OF VARIOUS NUCLEIC ACIDS.

	C.	H	N.	P.	O.	Base.
I. Thymonucleic acids of animal origin:						
1 Fisch sperm:						
a Salmon (Miescher and Schmiedeberg)	37.8	4.5	15.8	9.7	33.2	....
b Gadus (Levene)	34.8	5.2	16.8	9.1	...	....
c Homo (Katsuji and Inouye)	37.5	4.4	16.0	9.7	...	....
d Maifisch (Levene and Mandel)	36.3	5.0	15.9	8.1	...	....
2 Pancreas:						
a Ivar Bang	34.2	4.4	18.2	7.7	35.6	....
b v. Fürth, and Jerusalem	29.2	4.3	11.6	6.9	...	Cu = 14.2
3 Spleen (Levene)	37.8	4.8	16.5	8.99	...	....
4 Mammary gland (Levene and Mandel)	34.7	4.4	15.6	8.5	...	....
5 Intestinal wall (Katsuji Inouye)	37.5	4.8	15.5	9.4	...	....
6 Thymus gland:						
a (Ivar Bang)	35.8	4.2	15.3	9.3	...	Na — 6.25

---

[1] Altmann, "Über Nukleinsauren," *Arch. f. Anat. u. Physiol. Physiol. Abt.*, 1889, 524. Miescher, *Verhand. der naturforschenden Ges. in Basel*, 1874, 6, 138; *Arch. exp. Path. Pharm.*, 37, — (1896). Schmiedeberg, *Arch. exp. Path. Pharm.*, 43, 57 (1900). Kossel u. Neumann, *Ber.*, 27, 2215, (1894), Neumann, *Arch. Anat. und Physiol. Physiol. Abt.*, 1899, 552. Bang, *Z. physiol. Chem.*, 26, 133 (1898–9). Haiser, *Monatsh. Chemie*, 16. Levene, *Z. physiol. Chem.*, 32, 541 (1901); 37, 402 (1902–3); 45, 370 (1905).

	C.	H.	N.	P.	O.	Base.
b (Kostytschew)	31.4	4.6	12.8	7.6	...	Ba — 17.5
c (Herlant)	37.53	4.93	16.48	9.63	..	....
d (Schmiedeberg)	35.82	4.14	14.68	9.17	..	.....
II. Guanylic acid (animal origin):						
a Ivar Bang	34.28	4.39	18.21	7.64	34.48	.. ...
b Levene and Mandel	36.35	4.95	18.65	6.15	33.90	.. . .
III. Plant nucleic acid:						
1 Yeast:						
a Herlant	33.7	4.1	14.8	8.69	..	Cu — 16
b Levene	34.97	4.41	15.21	8.6	..	. ...
2 Wheat embryo (Osborne and Harris)	33.1	4.2	14.9	8.1	...	....

In adopting an empirical formula for the nucleic acids the individual investigators were guided not only by the analytical figures, but also by considerations of a speculative nature based to some extent on information obtained on partial or complete hydrolysis of the acids. The basis for the speculations of the different workers varied considerably. This led to a great divergence in the views on the empirical formula of nucleic acid. The following table contains some illustrations of it:

	C.	H.	N.	O.	P.
Schmiedeberg[1] (spermnucleic acid)	40	56	14	26	4
Steudel[2] (thymus nucleic acid)	43	57	15	26	4
Levene[3] (spleen nucleic acid)	54 43	71 55	20 15	37 31	5 4
Osborne and Harris[4] (wheat embryo nucleic acid)	42	62	16	31	4
Kossel[5] (yeast nucleic acid)	17 25	26 36	6 9	14 20	2 3
Boas[6] (yeast nucleic acid)	36	52	14	24	4
Levene[7] (yeast nucleic acid)	38	50	15	29	4

The Components of Nucleic Acids.

It has been stated that the first knowledge of the chemical nature of nucleic acids was limited to the information that it was a conjugated phosphoric acid. The first work of Altmann was followed by that of Kossel. The efforts of this investigator were directed towards the analysis of the products of hydrolytic cleavage of nucleic acids. His first achievement was the discovery of purine bases in the molecule of nucleic acids. These bases can be obtained on cleavage of nucleic acids with very dilute solutions of mineral acids. Kossel further devised methods for the separation of the individual bases. He arrived at the conclusion that four purine bases, namely, adenine, guanine, hypoxanthine and xanthine, enter into the molecule of nucleic acids. This view, however, was later revised as it was established that only two purine bases, adenine and guanine, actually enter into the composition of nucleic acids. Hypoxanthine and xanthine are now regarded as secondary products.[1] However, it was evident from the figures obtained on elementary analysis of nucleic acids, that their molecule contained substances other than purine bases. On the basis of the observation that on hydrolysis with dilute mineral acids only the purine bases are liberated and the other components remain intact, there was advanced a theory that in nucleic acids the phosphoric acid is combined with a complex radicle forming a conjugated phosphoric acid, and that this in its turn combined with the purine bases. The manner of this combination was the subject of considerable discussion and disagreement.

---

[1] *Arch. exp. Path. Pharm.*, 57, 309 (1907).

[2] *Z. physiol. Chem.*, 46, 332 (1905).

[3] *Biochem. Z.*, 17, 120 (1909).

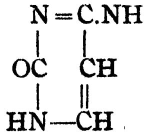
[4] *Z. physiol. Chem.*, 36, 85 (1902).

[5] *Arch. f. Anat. Physiol.*, p. 181 (1891).

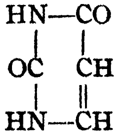
[6] *Arch. exp. Path. Pharm.*, 55, 16 (1906).

[7] *Biochem. Z.*, 17, 120 (1909).

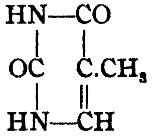
The efforts to elucidate the composition of the complex radicle resulted in the discovery of the following purine derivatives.[2]



Cytosine.



Uracil.



Thymine.

However, in order to obtain these substances it was necessary to resort to the hydrolysis by means of mineral acids of considerable concentration. This procedure caused many investigators to express doubt as to the presence of the pyrimidine bases in the nucleic acid molecule. The doubt was particularly great regarding the orgin of cytosine and uracil. R. Burian[3] with great persistence defended the view that these two bases took their origin in the partial cleavage of the purine ring. However, the majority of workers were inclined to consider cytosine also as a primary constituent of the molecule of nucleic acids, while uracil was considered a primary product in the acids of plant origin only.

Besides the purine and pyrimidine bases the molecule of nucleic acid was found to contain carbohydrates. The complex nucleic acids of animal origin contain a hexose, the exact nature of which is not yet established. The nucleic acid of plant origin and the simpler nucleic acid of the animal tissues contain a pentose. On the basis of the work of Neuberg[4] the pentose was considered *l*-xylose. However, very recently Jacobs and I have succeeded in isolating the substance in crystalline form. This made it possible to establish the true nature of the substance as *d*-ribose.[5]

As the methods of analysis had improved, and as approximately quantitative estimation of the components was made possible, it was found that in nearly all the acids the bases were present in approximately equimolecular proportions, that the number of molecules of phosphoric acid corresponded to that of the bases, and the number of molecules of carbohydrate was equal to that of phosphoric acid.[1]

---

[1] Levene, *Z. physiol. Chem.*, 45, 370 (1905). W. Jones and Austrian, *J. Biol. Chem.*, 3, 1 (1907).

[2] Kossel and Neumann, *Ber.*, 27, 2215 (1894). Ascoli, *Z. physiol. Chem.*, 31, 161 (1900–1). Kossel and Steudel, *Ibid.*, 37, 177 (1902–3). Levene, *Ibid.*, 37, 402, 527 (1902–3).

[3] R. Burian, *Ergebnisse der Physiol.* 3 *Jahrg.* 1 *Abt.*, 98 (1904); *Z. physiol. Chem.*, 51, 438 (1907). Steudel, *Z. physiol. Chem.*, 53, 508 (1907). Osborne and Heyl, *Am. J. Physiol.*, 20, 157 (1908). Levene and Mandel, *Biochem. Z.*, 9, 233 (1908).

[4] Neuberg, *Ber.*, 32, 3386 (1899).

[5] Levene and Jacobs, *Ibid.*, 42, 2102, 3247 (1909).

On the basis of these calculations, and on the basis of the numbers of the character of the bases entering into the molecule of the individual nucleic acids the following classification could be established:

1. Nucleic acids: Containing one purine base (no pyrimidine), a pentose and phosphoric acid. (Inosinic acid, guanylic acid.)
2. Nucleic acids: Containing two purine bases (guanine and adenine), two pyrimidine bases (cytosine and uracil) and phosphoric acid. (Phytonucleic acids.)
3. Nucleic acids: Containing two purine bases (guanine and adenine), two pyrimidine bases (thymine and cytosine), and a hexose and phosphoric acid. (Nucleic acid of animal tissue—thymonucleic acids.)

The Constitution of Nucleic Acids.

The early speculations regarding the constitution of nucleic acids were based on the results of partial hydrolysis by means of dilute acids or weak alkalies. Reference has been made already to the views expressed by Kossel.[2] By mere heating with water under increased pressure, this author thought he obtained a substance, which was free of purine bases, but contained all the other components of the original nucleic acid. The substance was named thymic acid. Nucleic acid was regarded therefore as a complex consisting of thymic acid and of purine bases. The author did not furnish any detailed information regarding the nature of thymic acid. Somewhat more definitely formulated was the view of Schmiedeberg. According to this author there existed a complex—nucleotin, this complex combined with phosphoric acid to form nucleotin phosphoric acid, and this acid in its turn combined with purine bases thus forming nucleic acid. Schmiedeberg ascribed to the nucleotin the formula $C_{30}H_{42}N_4O_{13}$. Alsberg,[3] working in Schmiedeberg's laboratory, actually succeeded in obtaining a substance which had the composition of the hypothetic nucleotin. However, these writers also failed to disclose the constitution of the complex radicle. In fact, they failed to furnish evidence that their substance was not a mixture composed of several cleavage products of nucleic acids.

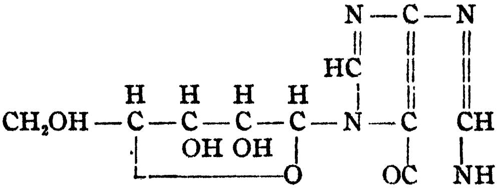
Results of actual significance for the interpretation of the structure of the nucleic acid were obtained only recently. The point of departure for the work was the study of inosinic acid by Levene and Jacobs. As has already been pointed out this acid is comparatively simple in its composition. It is composed of phosphoric acid, a pentose and hypoxanthine. Through prolonged action of dilute acid at the temperature of 50° it was possible to break up the molecule into hypoxanthine and a pentose-phosphoric acid.[1] This substance was obtained by Jacobs and myself in the form of its crystalline barium salt. This acid had all the properties of a conjugated phosphoric acid, and on cleavage yielded the phosphoric acid. The acid reduced Fehling's solution on heating without previous hydrolysis. It was concluded from this that in the molecule the phosphoric acid and the carbohydrate are bound in ester-form, and that the aldehyde group of the pentose phosphoric acid was free and that therefore in the inosinic acid the base and pentose were coupled in a glycoside union. This assumption was strengthened by the fact that inosinic acid was found to be very resistant towards the action of alkalies even at fairly high temperatures, and even on prolonged boiling the acid underwent only partial hydrolysis with formation of phosphoric acid and of the complex: pentose-base. Furthermore, it wasfound that by hydrolysis at nearly neutral point the conditions for the reaction were more favorable and it was possible in this manner to isolate and to identify the pentoside-inosine ($C_{10}H_{12}N_4O_5$). On the basis of this we concluded that the order of combination of the components in the molecule of the inosinic acid was established. I could add here that only on hydrolysis of the pentoside was it possible to obtain the crystalline sugar which was identified as *d*-ribose. The structure of the complex pentose-hypoxanthine may be represented in the following manner:

---

[1] Schmiedeberg, *Arch exp. Path. Pharm*, **46**, 57 (1900). Kossel u. Neumann, *Ber.*, **27**, 2215 (1894). Kossel u. Steudel, *Z physiol. Chem.*, **37**, 119, 120, 121, 131, 177 (1902–3); **145**, 377 (1903); **38**, 49. Ascoli, *Ibid.*, **31**, 161 (1900–1). Steudel, *Ibid.*, **42**, 165 (1904); **43**, 402 (1905); **44**, 157 (1905); **46**, 332 (1905); **48**, 425 (1906). Osborne and Harris, *Ibid.*, **36**, 85 (1902). Jones, W., and Austrian, *J. Biol. Chem.*, **3**, 1 (1907). Levene. *Z. physiol. Chem.*, **37**, 402, 527 (1902–3), **38**, 80 (1903); **39**, 4, 479 (1903); **43**, 199 (1904); **45**, 370 (1905). Levene and Stookey, *Ibid.*, **44**, 404 (1904). Mandel u. Levene, *Ibid.*, **46**, 155 (1905); **47**, 140 (1906). v. Fürth u. Jerusalem, *Beiträge Chem. Physiol. u. Pathol.*, **10**, 174 (1907).

[2] Kossel and Neumann, *Z. physiol. Chem.*, **22**, 74 (1896–7).

[3] Schmiedeberg, *Arch. exp. Path. Pharm.*, **43**, 57 (1900). Alsberg, *Ibid.*, **51**, 239 (1904).



The same substance had been found by Haiser and Wenzel in beet extract.[2]

Regarding the place of the purine base which entered into union with the sugar, there still remains only the evidence of Burian that place 7 is attached to the sugar and no information exists regarding the place of the hydroxyl in the pentose that is coupled with the phosphoric acid.

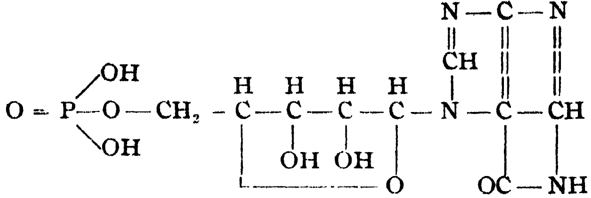
The following step in the progress of the work was the application of the experience obtained on inosinic acid to the other nucleic acids. Jacobs and I next directed our attention to the remaining acid of comparatively simple composition, namely guanylic acid. Employing the same methods of hydrolysis as applied to inosinic acid, we obtained guanosine ($C_{10}H_{13}N_5O_5$), a substance analogous to inosine; it possessed nearly the same crystalline form, differed in its physical constants, and on hydrolysis gave guanine and the same pentose as the inosine, namely *d*-ribose. This pentoside had the same properties as inosine in its behavior towards alkalies and acids.[3] For the sake of convenience we named the substances of this order "nucleosides" and the combination of the nucleoside and phosphoric acid we named "nucleotides." Thus according to that nomenclature inosine and guanylic acid were to be regarded as mononucleotides of the following structure:

---

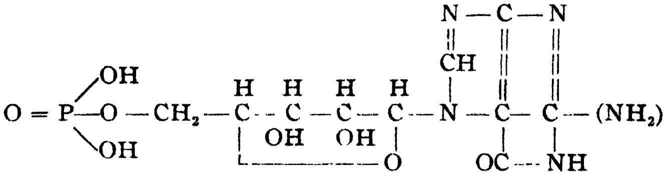
[1] *Ber.*, 44, 2703 (1908).

[2] Haiser and Wenzel, *Monatsh. Chem.*, 29, 157 (1908)

[3] *Ber.*, 42, 2474 (1909).

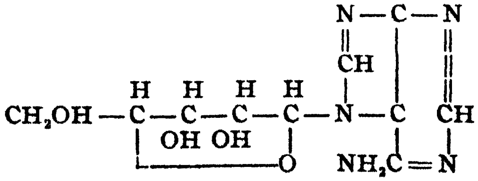


(Inosinic acid)



(Guanylic acid.)

The further application of the same methods to a more complex nucleic acid, to that of the yeast, led to the conviction that this also was composed in the same manner. Thus the same nucleoside-guanosine, as obtained from guanylic acid, was also found on hydrolysis of the yeast nucleic acid. When the proper conditions are observed the nucleoside can be chilled out and a nearly quantitative separation accomplished. In the filtrate from this nucleoside other substances of the same nature were expected. On the basis of considerations expressed by me in an earlier article on the composition of the yeast nucleic acid the molecule of the acid is composed of four nucleotides and therefore four nucleosides should be found on cleavage of the substance. The work in that direction is of comparatively recent date, and a second nucleoside has already been obtained from the mother liquor of guanosine.[1] The second nucleoside has practically the same crystalline appearance as inosine or guanosine, and differs from these two only by its physical constants and by the fact that on hydrolysis it yields in place of guanine the base adenine, and is, therefore, named adenosine. Also on hydrolysis of this nucleoside the crystalline *d*-ribose is obtained. The substance therefore had the following structure:



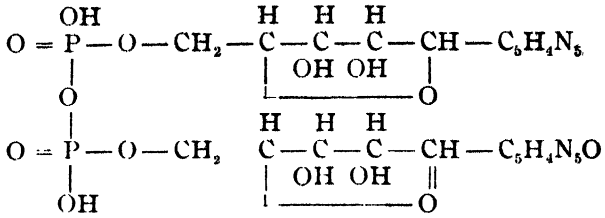
It possesses the melting point of 229° and the rotation: $[\alpha]_D = -67.30°$.

On the ground of this the structure of the yeast nucleic acid may be presented in the following manner:[2]

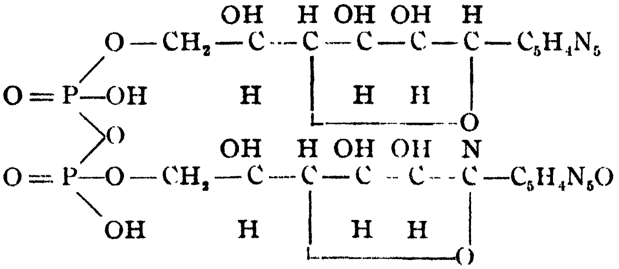
---

[1] Levene and Jacobs, *Ber.*, 42, 2703 (1909).

[2] Bloch, *Zeitsch.*, 120, 17 (1909).



All this work is of comparatively recent date so that as yet it could not have been extended to the analysis of thymonucleic acid. But evidence had been furnished that this substance also has a structure analogous to that of the yeast nucleic acid[1] In fact considerations based on the work on thymus nucleic acid were the first that led to formulating the structure of the complex nucleic acid as a polynucleotide, of which the individual mononucleotides were composed of phosphoric acid, sugar and base. Levene and Mandel have on hydrolysis of the spleen nucleic acid with dilute sulphuric acid obtained a substance which had the elementary composition ($C_{11}H_{17}N_2PO_{10}$) of a complex consisting of phosphoric acid, hexose and thymine. On cleavage with 25 per cent. sulphuric acid this body gave rise to phosphoric acid, levulinic acid and thymine. This assumption is in harmony with subsequent discoveries on the simple nucleic acid and on the yeast nulceic acid, and one feels justified in formulating the structure of thymonucleic acid in the following manner:



Thus the details in the structure of the molecule of nucleic acids are not yet known. But some general information is already obtained and the route is singled out, by which the solution of the problem will be reached. An indication is given for a point of departure for the work on the synthesis of these substances. Work in that direction is now in progress in our laboratory.

THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH,
NEW YORK CITY.

NEW BOOKS.

General Inorganic Chemistry. By CHARLES BASKERVILLE, Ph.D., Professor of Chemistry in the College of the City of New York. Boston, Mass.: D. C. Heath & Co. 1909. pp. vii + 357.

This book is of considerable interest as Professor Baskerville has departed from what has become the more or less standard method of presenting the facts of inorganic chemistry. The compounds described are not classified according to the metals which they contain, but according to the negative element which is present, or the acid from which they are derived. The elements are first considered, and then the oxides, sulphides, nitrates, sulphates, etc. The classification within these groups is according to the Periodic Law.

---

[1] *Ber.*, 41, 1905 (1908).

In the first chapter the student is introduced to chemical phenomena through experiments, which are described in detail These are selected to illustrate the fundamental concepts and laws of chemistry, which are appropriately emphasized. A brief chapter on the chemical elements follows, and then certain typical elements and compounds, together with their more important reactions are described at some length. Chapters are devoted to hydrogen, oxygen, water, the halogens, the halogen acids, alkali metals, nitrogen and ammonia, the air, carbon, carbon hydrides, carbon oxides, and valence. A study of these chapters prepares the student for the more logical treatment of the elements and compounds which follows. The Periodic Law is next discussed in some detail, and then the elements are described according to the relationships indicated by the law. The compounds are next considered in the order, halides, oxides, hydroxides, sulphides, hydrosulphides, carbonates, silicates, nitrogen oxides and hydroxides, sulphates, oxides and sulphides of manganese, oxides and sulphides of Group VII, binary compounds of Group IV and V, and compounds of carbon and nitrogen. There are unusually full chapters on radium and alloys.

The novel order of treatment which has been adopted has many apparent advantages and some disadvantages. Among the advantages is the readiness with which relationships between compounds of analogous composition can be pointed out, and the effect of the nature of the more positive element in a compound on reactivity and general chemical properties can be emphasized. Among the disadvantages is one of pedagogical importance. In the usual method of presenting compounds according to the metal which they contain, the discussions of oxides, sulphides, nitrates, etc., which come at intervals, make it possible to review frequently, in a brief manner, the facts already acquired. Repetition is an important factor in memory. According to the author's arrangement a great many related facts are learned at one time, and then more or less dismissed. The proof of the method is in its application, and according to the author, the method has led to successful results with a large number of students, over a period of several years.

The arrangement of facts in the way adopted has led to the description of a great many compounds which are not ordinarily considered in elementary textbooks. The book contains a mass of facts, stated very briefly. Although the text contains but 336 pages, the index covers 20 pages, each containing two columns.

The theoretical considerations are contained in two chapters placed in about the middle of the book: one on molecular weights (six pages), and one on the theory of electrolytic dissociation (five pages). In addition, there are a few brief references to such subjects as valence, reversible reactions, etc., scattered throughout the text. The theory appears to be given for the sake of the theory itself, and not on account of its value in interpreting chemical phenomena; little application is made of it in the treatment of compounds or reactions which are discussed in subsequent chapters.

The book is strikingly original and will, no doubt, appeal to many teachers. A student who has mastered its contents will know more facts of inorganic chemistry than can be learned by a study of many books twice its size. JAMES F. NORRIS.

Experimentelle Untersuchungen über Atomgewichte. VON THEODORE WILLIAM RICHARDS und seinen Mitarbeitern, 1887–1908. Mit 34 Abbildungen im Text Deutsche Ausgabe besorgt von J Koppel. Hamburg und Leipzig. Verlag von Leopold Voss. 1909 vi + 890 pp. Price, 35 marks.

A felicitous outcome of the delivery of a course of lectures in the University of Berlin by Professor Richards has been the publication of this substantial and important volume. About a fifth of its pages now appear for the first time in a German translation; the matter reprinted from a previous translation has been revised only to make it more faithful to the English original.

The first article is entitled "Die in Harvard ausgeführten Atomgewichtsbestimmungen"; the included bibliography gives the titles of 63 papers. Four of these contain the work of Cooke on antimony and of Huntington on cadmium, and antedate Richards' activity. Nine of the more recent do not mention his name as author. Of the remainder, 43 papers, filling 850 pages of this reprint, bear his name, and 19 of them, with their 330 pages, bear his name alone. These 43 together with three others needed for completeness of presentation, contain determinations of the atomic weights of no less than 19 elements: a magnificent body of work of the highest attainable accuracy.

EDWARD W. MORLEY.

Treatise on Qualitative Analysis. By J. F. SELLERS. Second revised edition, 173 pp. Ginn & Company. 1909. Price, $1.00.

Treatise is the proper title for this little work. It deals with qualitative analysis from all sides. Almost half of the book is taken up with theoretical considerations, explanations of analytical operations and additional notes. The application of physical chemistry to analytical chemistry is developed strongly and the presentation of this part is made very clear and attractive.

The part devoted to the detection and separation of the metals and acid radicles covers about the same ground that is included in most of the smaller works on this subject. The value of making comparisons between reactions brought about by the same reagent acting upon different solutions is left for the student to see for himself, it is not brought out here.

For training "future chemists" this book is inadequate, but foi students taking the course in a general way it is remarkably well adapted as it points out plainly that there is something to qualitative analysis beside color and solubility of precipitates, and the separation of the "six groups," a point entirely missed in many courses and most books. O. L. SHINN.

A Manual of Qualitative Analysis. By J. F. MCGREGORY. 133 pp Ginn & Company 1909 Price, $1.00.

This differs from most books on this subject in the arrangement. Groups and group reactions are not spoken of until all of the metals and the acid radicals have been studied separately. The groups are only discussed in the line of separations and the comparisons between the different metals are not made apparent. This method of treatment appears to multiply isolated facts and add confusion to the mind of the student. The term ion and the theory of dissociation are not used, and the old term radical is retained. The use of tables or schemes for group separations is condemned but one method of separating each group is described in the text.

The author states in the introduction that the book is not designed for those who intend to become chemists, but for those who can spend but a short time on this subject. For such students it would be a satisfactory book. O. L. SHINN.

An Introduction to Chemical Analysis for Students of Medicine, Pharmacy and Dentistry. By ELBERT W. ROCKWOOD, M.D., Ph.D. Third edition, illustrated, 247 pages. Philadelphia: P. Blakiston's Son & Co. Price, cloth, $1.50 net.

The first edition of this excellent laboratory guide was reviewed in THIS JOURNAL, **24,** 287. This third edition contains some new matter, and is especially characterized by the attention paid to the ionic interpretation of reactions. The preparation of a satisfactory book for a special class of students who have but a limited time to devote to chemistry is not an easy problem under any conditions; in the case of a work for medical students which must be full enough to prepare for physiological chemistry the difficulty is very great. Medical courses are already badly overcrowded.

The present book does not make any undue requirement on the time of the medical student, or call for more work than he should be expected to cover in his preparation for medicine. It presents a good outline of qualitative analysis and the minimum of the theory and practice of volumetric methods which may be considered necessary to fit the student for practical applications in later years of the course. There are also sections on the analysis of water and on the detection of poisons, and a long section on the identity tests for a considerable number of organic substances. The mechanical work on the book is excellent..

J. H. LONG.

Quantitative Chemical Analysis: Adapted for Use in the Laboratories of Colleges and Schools. By FRANK CLOWES, D.Sc., Lond., and J. BERNARD COLEMAN, A.R.C.Sc., Dublin. 8th Ed., 565 pages. P. Blakiston's Son & Co., Philadelphia. 1909. Price, $3.50 net.

The fact that this book has passed through eight editions (the first edition appeared in 1891) is a good indication of the favor with which it has been received. Indeed, the work is a standard in England, and here in America it has met with no small amount of success. Barring the translation of the Fresenius by Cohn, we know of no work on quantitative analysis in the English language which contains so much useful reliable and varied information. The text of the recent edition has been thoroughly revised, the type has been reset, and many improvements and additions have been made. The subject matter is arranged in eight parts, which are subdivided into eighteen sections: Part I is devoted to preliminary and general operations, Part II to gravimetric analysis, Part III to volumetric analysis, Part IV to complex quantitative estimations, Part V to the analysis of organic substances and the methods for determining molecular weights, Part VI to gas analysis, Part VII contains the results of a number of typical analyses as well as a fine set of reference tables, and Part VIII treats of the preparation of gases, the use of compressed gases, the distillation of water, etc. It also embraces a list of books for reference.

Among the additions of new matter we note in particular a section on the analysis of oils, fats and waxes, a number of electrolytic methods for determining some of the metals, and a description of, and the directions for using, the bomb calorimeter for coal valuation.

The book has a pronounced English flavor. It is written along conservative lines, theoretical matters have been omitted, and only those methods have been described which the authors regard as truly useful and well established. From the standpoint of the reviewer there are, in certain cases, methods of separation and determination which are superior to those cited by the authors. As examples he would mention Neher's admirable method for separating arsenic from antimony, Classen's electrolytic method for separating antimony from tin, and Penfield's device for determining water in rocks and minerals. We notice that in discussing the operation of filtration no mention is made of the Neubauer crucible. Further, the reviewer does not think that sufficient attention has been paid to the determination of silica in the silicates. The names of the discoverers of methods are only occasionally given, and no direct references to the chemical literature accompany the descriptions of processes. It is rather remarkable that in the list of books and journals Mohr's classic work on volumetric analysis and Fresenius' *Zeitschrift* find no mention. These, however, are minor shortcomings when we consider the excellence of the book as a whole. It is essentially a *practical* treatise on analysis, wide in scope, clear in its descriptions, and generally reliable in its methods. The type and paper are good, and the book is well bound. It is also provided with a good index. We welcome the appearance of this 8th edition, and take pleasure in warmly recommending it not only to teachers and students, but to analysts in general.

LEROY W. MCCAY.

Anleitung für das organisch präparative Praktikum. FRANZ W. HENLE. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1909. 8vo. 176 pp., 43 figs.

The attempt has been made, and that quite successfully, to present each preparation not as an individual synthesis but rather as a type of a general class of reactions. This is partially accomplished by the method of presenting the experimental directions but even more by the numerous citations to the original literature discussing the typical reactions of the class of substances under discussion. It is the opinion of the reviewer that the author has made plain to the student the need for the use of the original literature and thereby there will be much less occasion for the almost universal complaint that students engaged in organic preparations do not recognize the importance of reading the original literature.

Coming as it does from Thiele's laboratory at Strassburg, one expects, and finds, it to be thoroughly up to date in the references to the theory of the reactions as well as in the inclusion of examples of the Grignard, Sabatier and other modern syntheses.

It is one of the best of the more advanced manuals and like the others (Fischer, Gatterman, etc.) it will probably give its best service when preceded by a *short* course in which the simpler preparations of the aliphatic series are studied.

RALPH H. MCKEE.

Kolloidchemische Beihefte. By DR. WO. OSTWALD. Volume I, Nos. 1 and 2 Theodore Steinkopff, Dresden. To subscribers of the Kolloid-Zeitschrift 1 M., single volumes 1.20 M.

The object of this publication is to collect together and to present as early as possible the most important general articles on colloids. This is to be a supplement to the Kolloid-Zeitschrift. It should enable those who wish to follow the general advance of the subject to do so without having to discover or recognize for themselves the most important papers for that purpose. Thus, the monographs of Wolfgang Ostwald will differ from those of William Ostwald by being confined to a single subject and by being published as nearly as possible at the time of the completion of the experimental work.

W. R. Whitney.

Metallographie: Ein ausführliches Lehr-und Handbuch der Konstitution und der physikalischen, chemischen und technischen Eigenschaften der Metalle und metallischen Legierungen. Dr. W. Guertler. Erster Band: Die Konstitution. Heft. I., Berlin, Gebrüder Borntraeger. 1909. 80 pp. Price, M. 4.20.

Dr. Guertler has planned a comprehensive treatise on metallography. In this volume, which deals almost exclusively with the theoretical side of the subject, he discusses the constitution of binary alloys. After reviewing the early development of the science, equilibrium diagrams of binary mixtures are discussed from the point of view of the phase rule, solid solutions and compounds are studied, and the cooling curves of the alloys manganese-iron, iron-cobalt, and nickel-cobalt are considered in detail.

It is difficult to discuss in detail so small a part of an extensive treatise, but Dr. Guertler is especially well fitted to undertake a comprehensive work such as he has planned, and so far he has succeeded admirably. The book will be difficult for all except those who have had considerable training in physical chemistry. The discussion of some of the diagrams seems unnecessarily complicated, and it is believed that the practical methods of metallography should have been discussed as early as possible so as to make clear the manner of establishing a complete diagram. The book is excellently printed and is well provided with marginal references to the text.

Henry Fay.

The Elements of Metallography. By Rudolf Ruer. Translated by C. H. Mathewson. First edition. New York: John Wiley & Sons. 8vo. xiv + 342 pp., ill. Cloth, $3.

The book is divided into two parts, Theory and Practice. In Part 1 there are four chapters dealing with: *One-component system*, transformations and heterogeneous equilibria. *Two-component systems*, the different cases of various solubility in the liquid and solid states, without and with polymorphous transformations or the formation of chemical compounds. The different cases are illustrated by typical alloys mostly from work done at Goettingen. Supplementary sections are given on methods of determination of equilibrium curves and methods of investigation of solidified mixtures. *Three-component systems*, insoluble in solid state; completely soluble in solid state; phase rule.

Part 2 deals with methods of thermal investigation, heating apparatus, cooling and heating curves and the like; investigation of structure, microscopic examination. At the end of the book there is a collection of references to binary fusion diagrams and an index of authors' names besides the usual index.

To those who are interested in metals and alloys, and their name is legion, this work will be very welcome. It is well written and the reader is led by easy steps through the various groups of alloys, each illustrated by diagrams, without being lost in some of the more intricate problems of physical chemistry on the way. Criticisms of the book are few. Of the few photomicrographs given some are excellent while others are indistinct. The collection of references at the end of the book is apparently incomplete, while the addition of sections on brasses and bronzes parallel to that on iron and carbon would have been of value to many general readers.

For such a book there is a great need and this one will undoubtedly be a welcome addition both for class work and the general reader.

WILLIAM CAMPBELL.

RECENT PUBLICATIONS.

ABEGG, R., UND AUERBACH, FR.: **Handbuch der anorganischen Chemie, in 4 Bänden.** 3 Bd. 2 Abt. Die Elemente der vierten Gruppe des periodischen Systems. Leipzig: S. Hirzel. Geb., 27 M.

ABEL, R.: **Bakteriologisches Taschenbuch, enthaltend die wichtigsten technischen Vorschriften zur bakteriologischen Laboratoriumsarbeit.** Würzburg: Curt Kabitzsch A. Stubers Verlag). 13 Aufl. Kl. 8°, 130 s. Geb., 2 M.

ARRHENIUS, SVANTE: **Theorien der Chemie.** Übersetzt von Alexis Finkelstein. 2 Aufl. Leipzig: 1909. Akademische. Verlagsgesellschaft m. b. H. 7.50 M.

AUTENRIETH, W.: **Die Auffindung der Gifte und stark wirkender Arzneistoffe.** Zum Gebrauch in chem. Laboratorien. Tübingen: J. C. B. Mohr. (Paul Siebeck.) 4 vollst. neubearb. Auflage. Gr. 8°, 286 s., geb., 8.60 M.

BAGSHAW, W.: **Elementary Photomicrography.** Second edition. Hiffe. 8°, 104 s., 2 s.

BAILEY, C. H.: **First Stage Inorganic Chemistry** (Theoretical). Fourth edition. W. B. Clive. 8°, 257 pp., 2 s.

BAIRD, H. C.: **The Practical Dry Cleaner, Scourer and Garment Dyer.** Edited by W. T. Brannt. 3d ed. rev. and enl. Phila.: H. Carey Baird & Co. $2.50.

BAUSOR, H. W.: **First Stage Inorganic Chemistry (Practical).** Revised edition. Clive. 1 s.

BEHRE, P.: **Ueber einige Adsorptionserscheinungen.** Hildesheim: August Lax. 8°, 69 s., 2 M.

BENNETT, H. G.: **The Manufacture of Leather.** Constable. 8°, 442 pp., 1 s, 6 d

BILTZ, H.: **Qualitative Analyse anorganischer Substanzen.** Leipzig: Veit & Co 3 Auflage. Geb., 2.40 M.

BINZ, PROF. DR. A.: **Chemisches Praktikum für Anfänger.** Mit Berücksichtigung der Technologie. Berlin: G. Reimer. 154 s., 4.80 M.

Birckenbach, L.: **Die Untersuchungsmetheden des Wasserstoffperoxyds.** Stuttgart: Ferd. Enke. 142 s., geb., 5 M.

Birnbaum, K.: **Leitfaden der chem. Analyse.** 8, verb. u. verm. Aufl. Bearb. von E. Dieckhoff. Leipzig: Joh. Ambr. Barth. 8°, 198 s., geb., 4.80 M.

Bornemann, G.: **Stöichiometrie.** Grundzüge der Lehre von den chemischen Berechnungen. Leipzig: 1909. S. Hirzel. Geb., 4 M.

Bornemann, K.: **Die binären Metalllegierungen.** Teil I. Halle a/S: Wilh. Knapp. 7 M.

Bothas, Ludwig: **Massendestillation von Wasser.** Berlin: J. Springer. 53 s., 2 M.

Caven, R. M.: **Systematic Qualitative Analysis for Students of Inorganic Chemistry.** Blackie. 8°, 250 pp., 3 s., 6 d.

Chaplet, A., and Rousset, H.: **Les succédanés de la soie. Les soies artificielles.** 8°, 168 s., 3 Fr.

Clowes, F., and Coleman, T. B.: **Quantitative Chemical Analysis.** 8th ed Churchill. 8°, 590 pp., 10 s. 6 d.

Cohn, Dr. L.: **Chemistry in Daily Life.** Popular lectures. Translated by M. P. Muir. 4th ed. 8°, 304 pp. Price, 6 s.

Coops, Dr. G. H.: **Übersichtliche Darstellung des zweiten Hauptsatzes der Thermodynamik und der daraus herzuleitenden Folgen.** Gröningen, Holland: P. Noordhoff.

Crato, E.: **Massanalyse.** Leipzig: J. A. Barth. Geb., 7.80 M.

Danneman, F.: **Leitfaden für den Unterricht im chemischen Laboratorium.** 4 Aufl. Hannover: Hahn'sche Buchh. 86 s., geb., 1.80 M.

Davis, A. C.: **Portland Cement.** 2nd ed. Tawcet: Woodford. 8°, 410 pp., 15 s.

Denz. Ferd: **Die Holzverkohlung und der Köhlereibetrieb.** Wien: Moritz Perles. Geb., 12 M.

Dichmann, K.: **Der basische Herdofenprozess.** Berlin: Julius Springer. 7 M.

Doelter, C.: **Das Radium und die Farben. Einwirkung des Radiums und ultravioletter Strahlen auf organische und anorganische Farben sowie auf Mineralien.** Dresden: Th. Steinkopff. 8°, geb., 5 M.

Donath, Prof. Ed.: **Ueber den Ersatz des Schwefelwasserstoffs in der qualitativen chemischen Analyse.** Leipzig: S. Hirzel. 8°, 63 s.

Emery, F. B.: **Elementary Chemistry.** London: Williams & Norgate. 8°, 8 s., 6 d.

Erdmann, H.: **Die Fixierung des Luftstickstoffs und ihre Bedeutung für Ackerbau und Industrie.** Bearb. von M. von Unruh. Leipzig: H. A. Ludwig Degener. 1 M.

Euler, H.: **Grundlagen und Ergebnisse der Pflanzenchemie.** Braunschweig: F. Vieweg & Sohn. Gr. 8, geb., 9 M.

Felsen, F.: **Der Indigo und seine Konkurrenten.** Berlin: Verlag für Textilindustrie. 4, 76 s., geb., 10 M.

Felt, W.: **Ueber die Darstellung des Chlorkaliums aus Hartsalz.** Halle a/S: Wilh. Knapp. 2.40 M.

Fenton, H. J. H.: **Outlines of Chemistry with Practical Work.** 8°, 384 pp., 9 s.

FICHTER, PROF. DR. F.: **Uebungen in quantitativen chemischer Analyse.** Basel: Verlag von F. Reinhardt. 139 s., 2.40 M.

FISCHER, BERNHARD: **Lehrbuch der Chemie für Pharmazeuten.** Sechste Auflage. Neu bearbeitet von Dr. Georg Frerichs. Stuttgart: 1909. Verlag von Ferdinand Enke.

FOERSTER, F.: **Beiträge zur Kenntniss des elektrochemischen Verhaltens des Eisens.** Halle a/S: W. Knapp. 3.20 M.

FRITSCH, J.: **Fabrication des engrais chimiques.** Paris: H. Desforges. 8°, 20 Fr.

GADAMER, J.: **Lehrbuch der chemischen Toxikologie und Anleitung zur Ausmittelung der Gifte, für Chemiker, Apotheker und Mediziner.** Bearb. unter. Mitwirkung von W. Herz und G. Goebel. Göttingen Vandenhoeck & Ruprecht. Lex.-8°, 725 s., geb., 20 M.

GENTELE, J. G.. **Lehrbuch der Farbenfabrikation.** 3 umgearb. und verm. Aufl. von A. Buntrock. 2 Bd. Die Mineralfarben 17 M.; 3 Bd. Die Lackfarben. 6 M. (Bd. 1, Die Erdfarben, erschien 1906). Preis, fur Bd. 1-3, geb., 30 M. Braunschweig: F. Vieweg & Sohn.

GERKE, O.: **Repetitorium der pharmazeutischen Chemie.** Magdeburg: Schallehn & Wollbrück 1 M.

GIESEN, W.. **Spezialstähle in Theorie und Praxis.** Freiberg i/S Craz & Gerlach 8, 3 M

GLIKIN, DR. W.: **Biochemisches Taschenbuch.** Berlin. Gebr. Bornträger.

GODFREY, H.. **Elementary Chemistry.** New York Longmans, Green & Co. $1.10.

GRAFFIGNY, H. DE. **La métallurgie électrique.** 8, 208 s., 1.50 Fr.

GRÜNWALD, J.: **The Theory and Practice of Enamelling on Iron and Steel.** London: A. Griffin & Co.

GUERTLER, DR. W.: **Metallographie.** 1 Band. Die Konstitution. Berlin: Verlag. Gebr Borntraeger. Heft. 1. 80 s

HAENIG, A.: **Der Graphit.** Wien. A. Hartlebens Verlag. Geb. 4.80 M.

HAENIG, A.. **Der Schmirgel und seine Industrie.** Wien: A. Hartleben's Verlag. Geb. 3.80 M.

HALL, A. D.: **Fertilizers and Manures.** London: J. Murray. 8°, 5 s.

HANNEKE, P.: **Die Herstellung von Diapositiven.** II Auflage. Berlin: 1909 Verlag von Gustav Schmidt (vorm. R. Oppenheim). 2.50 M.

HARTING, H.: **Optisches Hilfsbuch für Photographierende.** Berlin: Gustav Schmidt. Gr. 8, 180 s.

HASTERLIK, DR. ALFRED: **Der Tafelsenf (Mostrich) und die technische Verwertung der Senfpflanze.** Wien und Leipzig: 165 s., 3 M.

HEBING, C.: **Oelfarbe und Oelfarbenanstriche.** München: Georg D. W. Callwey. 8, 152 s., 4 M.

HEIL, A., AND ESCH, W.: **Manuel pratique de la fabrication du caoutchouc et du produits qui en dérivent.** 8°, 248 s., 12.50 Fr.

HLASIWETZ, DR. H.: **Anleitung zur quantitativen chemischen Analyse.** 14 Auflage, durchgesehen von Dr. G. Vortmann. Leipzig und Wien: Franz Deuticke. IV, 51 s., 1 M.

IDDINGS, J. P.: **Igneous Rocks, Vol. I. Their Chemical and Mineral Composition.** New York: John Wiley & Sons. $5.00.

JABS, ASMUS: **Torfkoks und Kraftgas.** Berlin: A. Seydel. 1 M.

JÄNECKE, DR. E.: **Gesättigte Salzlösungen vom Standpunkt der Phasenlehre.** Halle a/S: W. Knapp. IX und 187 s., 9 M.

JÖRGENSEN, ALFRED: **Die Mikroörganismen der Gärungsindustrie.** Fünfte, neubearbeitete und vermehrte Auflage. Berlin: 1909. Verlag von Paul Parley. 485 s., 12 M.

KAHLENBERG, L.: **Outlines of Chemistry; a Text-book for College Students.** New York: MacMillan. 2.60.

KARSTEN, J., UND OLTAMUS, F.: **Lehrbuch der Pharmakognosie.** 2 Aufl. Jena: Gustav Fischer. 358 s., geb., 10 M.

KEDESDY, E.: **Die Sprengstoffe. Darstellg. u. Untersuchg. der Sprengstoffe u. Schiesspulver.** Hannover: 8°, VII, 283 s., geb., 4.60 M.

KELLAS, A. M.: **Introduction to Practical Chemistry for Medical, Dental and General Students.** H. Frowde. 8°, 270 pp., 3 s., 6 d.

KING, A. S.: **An Electric Furnace for Spectroscopic Investigations, with Results for the Spectra of Titanium and Vanadium.** Washington: Carnegie Institute.

KIPPING, F. S., AND PERKIN, W. H.: **Inorganic Chemistry. Part I.** Chambers. 8°, 320 pp., 3 s., 6 d.

KIRSKALT, U. HARTMANN: **Praktikum der Bakteriologie und Protozoologie.** 2 erweit. Aufl. 1 Teil: Bakteriologie. (Lex. 8, 111 s.) Jena: Gustav Fischer. Geb. 3.50 M.

KNORR, E.: **Leitfaden der Chemie für Brauer und Mälzer.** Leipzig: Eisenschmidt & Schulze. G. m. b. H. 8°, 390 s., geb., 8 M.

KRAFT, DR. ERNST: **Analytisches Diagnostikum. Die chemischen mikroskopischen und bakteriologischen Untersuchungsmethoden von Harn, Auswurf, Magensaft, Blut, Kot.** Leipzig: J. A. Barth. 405 s., 9 M.

KRÜSS, G., UND H.: **Kolorimetric und quantitative Spektralanalyse in ihrer Anwendung in der Chemie.** 2 verbesserte und vermehrte Auflage, bearbeitet von H. und P. Krüss. Hamburg: 1909. Leopold Voss. Gr. 8, 284 s., 8 M.

LANDOLT, H.: **Ueber die Erhaltung der Masse bei chemischen Umsetzungen.** Halle a/S: W. Knapp. 1.80 M.

LAUBENHEIMER, K.: **Phenol und seine Derivate als Desinfektionsmittel.** Wien: Urban & Schwarzenberg. Lex. 8, 156 s., geb., 8 M.

LEHNER, S.: **Die Kitte und Klebemittel.** 7 Aufl. Wien: A. Hartlebens Verlag. Geb., 2.60 M.

LIEBETANZ, F.: **Calciumcarbid-Fabrikation.** 3 Aufl. Leipzig: Askar Leiner. Geb., 3.70 M.

LINSCHMANN, H.: **Die Spiritusindustrie, ihre Technik, Steuern und Monopole.** Stuttgart: E. H. Moritz. Geb., 2.50 M.

LÖB, W.: **Einführung in die chemische Wissenschaft.** Leipzig: B. G. Teubner. Geb., 1.25 M.

LOCKEMANN, G.: **Die Beziehungen der Chemie zur Biologie und Medizin.** Heidelberg: Carl Winters Universitäts-Buchhandlung. 80 Pf.

LÖSCHER, FRITZ: **Vergrössern und Kopieren auf Bromsilberpapier.** Dritte erweiterte Auflage. Bearbeitet von H. Löscher. Berlin: G. Smith.

MACFARLANE, W.: **Laboratory Notes on Iron and Steel Analysis.** New York: Longmans, Green & Co. $2.50.

Mees, C. E. K.: **An Atlas of Absorption Spectra.** Longmans.

Meyer, W.: **Ausgewählte Kapitel über Chemie.** I. Teil. Anorganische Chemie. 131 s. Preis, 2 M. II Teil. Organische Chemie. 47 s., 1.20 M. Berlin: Hermann Meusser.

Michaelis, Prof. Dr. L.: **Dynamik der Oberflächen. Eine Einführung in biologische Oberflächenstudien.** Dresden: 1909. Verlag von Th. Steinkopff. 4 M.

Michaelissen, Dr.: **Der Erhärtungsprozess der kalkhaltigen hydraulischen Bindemittel.** Dresden: Th. Steinkopff. 1.50 M.

Miller, J. B.: **Glasätzerei.** 4 Aufl. Wien: A. Hartlebens Verlag Geb., 2.60 M.

Minkowski, E.: **Ueber das Verhalten einiger aromatischer Essigsäure- und Glykollderivate tierischen Fermenten gegenüber.** München: Georg. C. Steinicke. 28 s., 80 Pf.

Mohr, Prof. Dr. Ernst: **Anleitung zum zweckmässigen Rechnen bei chemischen präparativen Orbeiten.** Braunschweig: 1909. Druck und Verlag von Friedr. Vieweg & Sohn.

Moor, C. G.: **The Recognition of Minerals.** Mining Journal. 8°, 231 pp., 7 s. 6 d.

Moor, C. G., and Partridge, W.· **Aids to the Analysis of Food and Drugs.** 3rd ed. Baillière. 3 s. 6 d.

Moraucé, E.: **Composition chimique des alcools d'industrie et des spiritueux.** 8°, 1.50 Fr.

Newell, L. C.. **A Course in Inorganic Chemistry.** London: D. C. Heath & Co. 8 s., 6 d.

Obermiller, J.: **Die orientierenden Einflüsse und der Benzolkern.** Leipzig: Joh. Ambr. Barth. Gr., 8, 144 s., 4 M.

Oesterle, O. A.: **Grundriss der Pharmakochemie.** Berlin: 1909. Verlag von Gebrüder Bornträger.

Oppenheimer, Prof. Carl: **Die Fermente und ihre Wirkungen.** Dritte völlig umgearbeitete Auflage. Leipzig: F. C. W. Vogel. 491 s., geb., 17.50 M

Orloff, J. E.: **Formaldehyd.** Leipzig: J. A. Barth. Geb., 11 M.

Osborn, T. B.: **The Vegetable Proteins.** Monographs on Biochemistry, edited by R. H. Aders Plimmer and F. G. Hopkins. New York: Longmans, Green & Co. $1.20.

Ostwald, W.: **Die Energie. Wissen und Können.** Band I. Leipzig: J. A. Barth. 167 s.

Ostwald, Wilh.: **Einführung in die Chemie.** Stuttgart: Franckh'sche Verlagshdlg., geb., 3 M.

Ostwald, Dr. W.: **Grundriss der Kolloidchemie.** Dresden: Theodor. Steinkopff. 12 M., geb., 13.50 M.

Ostwald, W.: **The Fundamental Principles of Chemistry:** An Introduction to All Text-books of Chemistry, authorized translation by Harry W. Morse. New York: Longmans. $2.25.

Ostwald, W., and Morse, H. W.: **Elementary Modern Chemistry.** Boston: Ginn. $1.00.

Otto, C.: **Eisenreduktion in Puddelofen.** Kattowitz: Gebr. Böhm. 0.80 M.

Parsons, C. L.: **Chemistry and Literature of Beryllium.** Easton, Pa.: Chemical Publishing Co. 180 pp. $2.00.

PARTHEIL, A.: **Lehrbuch der Chemie.** Organische Teil, Abteilung 1. Chemie der Fettkörper. Bonn Rh.: Carl Georgi. 8 M.

PFYL., B., UND RASENACK, P.: **Ueber die Verpuffungs- und Verbrennungsprodukte von Celluloid.** Berlin: Julius Springer. Lex. 8, 34 s., 2 M.

PHILIP, J C.: **The Romance of Modern Chemistry.** Seeley. 8, 348 pp., 5 s.

PICK AND CONRAD: **Die Herstellung von hochprozentigen Ferrosilicium im elektrischen Ofen.** Halle a/S: W. Knapp. 6.60 M.

PONTIO, MAURICE: **Analyse du caoutchouc et de la guttapercha.** Publication de l'encyclopédie scientifique des aide-mémoires. Paris: Gauthier-Villars, Masson et Cie.

PÖSCHL, DR. VIKTOR: **Die Härte der festen Körper und ihre physikalisch-chemische Bedeutung.** Dresden: Verlag von Th. Steinkopf. 8, 84 s., 2.50 M.

POULSSON, E.: **Lehrbuch der Pharmakologie.** Deutsche Originalausgabe von F. Leskien. Lepizig: S. Hirzel. Geb., 15.60 M.

PUYO, C.: **Der Oelfarben-Kopierprozess nach Rawlins.** Autorisierte Übersetzung von Dr. C. Stürenburg. Berlin: Gustav Schmidt. 8°, VI und 71 s.

QUEDENFELDT, DR. E.: **Die Praxis des Gummidruckverfahrens.** Leipzig: Edw. Liesegangs Verlag. 2 M.

RAKUSIN, M. A.: **Die Theorie der Färbung der natürlichen Erdöle und deren notwendige Konsequenzen.** Berlin: Verlag für Fachliteratur. G. m. b. H. Gr., 8, 29 s., 2 M.

REMSEN-SEUBERT: **Anorganische Chemie.** 4 Aufl. Tübingen: H. Larppsche Buchhandlung. Gr., 8, geb., 10 M.

REMSEN-SEUBERT: **Einleitung in das Studium der Chemie.** 4 Aufl. Geb., 7 M.

RICHARDS, TH., WILSON, J. H., AND GARROD-THOMAS, R. N.: **Electrochemical Investigation of Liquid Amalgams of Thallium, Indium, Tin, Zinc, Cadmium, Lead, Copper, and Lithium.** Washington: Carnegie Inst. 72 pp.

RICHTER, K.: **Zink, Zinn, und Blei.** 2 Aufl. Wien: A. Hartlebens Verlag. Geb., 4.05 M.

RIES, H.: **History of the Clay-working Industry in the United States.** New York: John Wiley & Sons. $2.50.

ROSSMÄSSLER, F. A.: **Die flüssigen Heizmaterialien und ihre Anwendung.** Wien: A. Hartleben's Verlag. Geb., 3.80 M.

ROTH, W. A.: **Exercises in Physical Chemistry.** Authorized tr. by A. T. Cameron. New York: D. Van Nostrand Co. $2.00.

ROUSSET, HENRI, ET CHAPLET, A.: **Les combustions industrielles. Le controle chimique de la combustion.** Paris: Gauthier-Villars. 263 s., 168 Abb.

SCHAEFER, F.: **Die wirtschaftliche Bedeutung der techn. Entwicklung in der Papierfabrikation.** Leipzig: Dr. W. Klinkhardt. 284 s., geb., 8 M.

SCHMIDT, HANS: **Die photographische Praxis.** Union: Deutsche Verlagsgesellschaft.

SCHMIEDERBERG, O.: **Grundriss der Pharmakologie in Bezug auf Arzneimittellehre und Toxikologie.** Leipzig: F. C. W. Vogel. 6 Aufl. Gr., 8, 611 s., geb., 12.75 M.

SCHOORL, N.: **Beiträge zur mikrochemischen Analyse.** Wiesbaden: C. W. Kreidel's Verlag, gr., 8, 160 s., 3.60 M.

SCHUMANN, A.: **Wie scheidet man Nickel am besten ab auf elektrolyt. Weg?** Kattowitz: Gebr. Böhm. 0.80 M.

Seubert, K.: **Internationale Atomgewichte. Nach den Festsetzungen des internationalen Atomgewichts Ausschusses herausgegeben.** (2 Bl.). Leipzig: Breitkopf & Härtel. Preis, 1 M.

Smith, J. C.: **Oxide of Zinc, its Nature, Properties and Uses.** Trade Paper Co. 8°, 112 pp., 3 s.

Sperber: **Anorganische Chemie.** Zürich: E. Speidel.

Spiegel, L.: **Chemische Konstitution und physiologische Wirkung.** Stuttgart: Ferd. Enke. Lex. 8, 96 s., 3.60 s.

Spilker, Dr. A.: **Kokerei und Teerprodukte der Steinkohle.** Halle: Wilh. Knapp. Bd. XIII, 3.60 M.

Step, Josef.: **Das Radium und seine Eigenschaften.** St. Joachimstal: Hugo Friedrich.

Stewart, A. W.: **Recent Advances in Physical and Inorganic Chemistry.** Longmans. 8°, 282 pp., 7 s., 6 d.

Surface, G. T.: **The Story of Sugar.** London: D. Appleton & Co. 8°, 3 s.

Svedberg: **Die Methoden zur Herstellung Kolloider Lösungen anorganischer Stoffe.** Ein Hand- und Hilfsbuch für die Chemie und Industrie der Kolloide. Dresden: 1909. Verlag von Theodor Steinkopff. 507 s.

Teichert, K.. **Methoden zur Untersuchung von Milch und Molkereiprodukten.** Stuttgart: Ferd. Enke. Gr., 8, geb., 12 M.

Tower, W. Sh.: **The Story of Oil.** Appleton. 8, 284 pp. Price, 4 s.

Uhlenhuth, P., und Weidanz, O.: **Praktische Anleitung zur Ausführung des biologischen Eiweissdifferenzierungsverfahrens mit besonderer Berücksichtigung der forensischen Blut- und Fleischuntersuchung, sowie der Gewinnung präzipitierender Sera.** Jena: Gustav Fischer. Lex. 8, 246 s., 6.50 M.

Uhlenhuth, X.: **Untersuchungen über "Antiformin," ein bakterienauflösendes Desinfektionsmittel.** Berlin: Julius Springer. Lex. 8, 61 s., 4 M.

Vogel, H. W.: **Photographie.** 2 vermehrte Auflage, bearbeitet von Hans Spörl. Braunschweig: F. Vieweg & Sohn.

Vogel, Dr. E.: **Taschenbuch der Photographie. Ein Leitfaden für Anfänger und Fortgeschrittene.** Bearbeitet von Paul Hanneke. Berlin: 1909. Verlag von Gustav Schmidt. 336 s.

Vrancken, E., et Aulard, A.: **Manuel de la fabrication du sucre de betterave a l'usage des praticiens.** Brüssel: Ramlot frères soeurs. 8, 10 Fr.

Wein, E.: **Das Kalisilicat (Phonolithmehl) als Kalidüngemittel.** Freising: Dr. Franz Paul Datterer & Co. Gr., 8, 90 s. Preis, 1.50 M.

Weinstein, Prof. Dr. B.: **Physik und Chemie in gemeinverständlicher Darstellung.** Zum Selbstunterricht und für Vorlesungen. 2 vollständig umgearbeitete und erweiterte Auflage. 1 Band. Allgemeine Naturlehre und Lehre von den Stoffen. Leipzig: 1909. Verlag von Johann Ambrosius Barth. 8, 272 s., 4.20 M.

Weisbach, Abb.: **Tabellen zur Bestimmung der Mineralien mittels ausserer Kennzeichen.** 8 Aufl. Bearb. von Fr. Kolbeck. Leipzig: Arthur Felix. Gr., 8, 121 s. geb., 4.40 M.

Wentzel, und Paech: **Photographisches Reisehandbuch.** Berlin: 1909. Verlag von Gustav Schmidt. 3 M.

Wirchowski, S.: **Einführung in die qualitative chemische Analyse zum Gebrauch bei den prakt. Uebungen im Laboratorium.** Wien: Josef. Safár. 2 M.

WIENER, O.: **Ueber Farbenphotographie und verwandte naturwissenschaftliche Fragen.** Leipzig· Joh Ambr. Barth. Gr., 8, 2.40 M

WINTERSTEIN, PROF. E., UND TRIER, G.: **Beilstein's Anleitung zur qualitativen Analyse.** 9 Aufl. Leipzig: J. A. Barth. 8°, 80 s., geb , 2.60 M

WOLLAND, H **Chemisches Praktikum (qualitative Analyse) für höhere Lehranstalten.** Wien Franz Deuticke.

WORDEN, DR. KONRAD: **Monographien über Angewandte Elektrochemie.** XXXI Band. **Electrolytische Zahler.** Halle a/S 1908. Verlag von Wilhelm Knapp. 166 s, geh., 9 M.

ZERR, G., UND RÜBENCAMP, R. **Handbuch der Farbenfabrikation.** 2 Aufl. Berlin· Union, Deutsche Verlagsgesellschaft. Geb., 30 M.

ZSIGMONDY, R · **Colloids and the Ultramicroscope.** London· Chapman & Hall. 8°. Price, 12 s., 6 d.

ZWICK, H **Hydraulischer Kalk und Portlandzement, ihre Rohstoffe, physikalischen und chemischen Eigenschaften.** 3 umgearb. Aufl , bearbeit. von Dr. A. Moye. Wien A. Hartleben. 8°, 238 s., geb., 5.3 M.

VOL. XXXII. MARCH, 1910. No. 3.

THE JOURNAL

OF THE

American Chemical Society

SEVENTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1909.

BY F W CLARKE.

Received February 2, 1910

The year 1909 has been marked by unusual activity in the determination of atomic weights, and much of the work done was of remarkably high quality. It is also noteworthy because of the publication, in German, of the collected papers by Richards and his colleagues in Harvard University.[1] The actual work of the year, including some data from 1908, may be summarized as follows:

Chlorine and Nitrogen.—The work of Guye and Fluss[2] on nitrosyl chloride, NOCl, appeared in December, 1908, too late for recognition in the report for last year. The weighed gas was passed, first over silver, which absorbed the chlorine; then over heated copper, which fixed the oxygen; and finally over calcium, which combined with the nitrogen. A complete analysis of nitrosyl chloride was thus effected, giving direct comparisons of nitrogen and chlorine with oxygen, independent of every other atomic weight. The following data were obtained, the actual weights being given in the first four columns:

NOCl.	N.	O.	Cl.	At. wt. N.	At. wt Cl.
0.5341	0.1142	0.1305	0.2893	14.000	35.470
0.4284	0.0916	0.1046	0.2319	14.012	35.472
0.7995	0.1710	0.1954	0.4331	14.002	35.464
0.5639	0.1204	0.1375	0.3048	14.010	35.468
0.5121	0.1095	0.1251	0.2773	14.005	35.466
			Mean,	14.008	35.468

---

[1] Experimentelle Untersuchungen über Atomgewichte, von Theodore William Richards und seinen Mitarbeitern. Hamburg und Leipzig, 1909.

[2] *J. chim. phys.*, 6, 733. The table given here is abbreviated from the tables as published by Guye and Fluss.

Scheuer[1] deduces the atomic weight of chlorine from the density of gaseous hydrochloric acid. Twenty-eight determinations are given, representing weighings in six different globes. The mean of all, for the weight of a normal liter of hydrochloric acid, is 1.63941 grams. From this figure Scheuer computes, by different methods, values for Cl between 35.442 and 35.454. He concludes that the atomic weight is very near 35.45.

The density, composition by volume, and compressibility of hydrochloric acid have also been determined, with great care, by Gray and Burt.[2] Three series of density determinations are given, with gas from different sources. The following figures give the weight of one liter of hydrochloric acid, at 0°, 760 mm., and at London:

I.	II.	III.
1.64053	1.64022	1.63950
1.64004	1.63999	1.64013
1.64020	1.63976	1.63984
1.63986	1.64083	1.64069
....	1.64030	1.64031
....	1.64021	1.64017
....	1.64027	1.64050
....	....	1.64051
....	....	1.63992
....	....	1.64001

Series I and II are subject to a small correction for gas adsorbed by the walls of the glass bulbs in which the weighings were made. Series III represents weighings in "quartz" glass, and do not need the correction. The final mean, reduced to Lat. 45°, gives for the weight of the normal liter, 1.63915 grams.

In order to determine the volumetric composition of hydrochloric acid, measured volumes of it were decomposed by heated aluminum, and the volume of hydrogen liberated was also measured. From two volumes of hydrochloric acid the following volumes of hydrogen were obtained.

1.00797	1.00781
1.00795	1.00779
1.00790	1.00787
1.00790	1.00798

Mean, 1.00790. Combining this figure with that given for the density, and with Morley's value for the atomic weight of hydrogen, 1.00762, Cl = 35.459. The compressibility measurements, which are too complex for reproduction here, gave with the density determinations, by the method of limiting densities, the value Cl = 35.461. The mean value, 35.460, is adopted by the authors.

---

[1] *Compt. rend.*, 149, 599. Scheuer's complete memoir (*Z. physik. Chem.*, 68, 575) was received too late for consideration here. Scheuer discusses his own data very fully, and finally combines them with the figures given by Gray and Burt. His final conclusion is that Cl = 35.466.

[2] *J. Chem. Soc.*, 95, 1633.

Nitrogen and Silver.—A new series of analyses of ammonium chloride is due to Richards, Koethner and Tiede.[1] The results, with all corrections applied, are as follows:

Weight NH_4Cl.	Weight AgCl.	At. wt. N.
2.02087	3.41469	14.009
2.23894	5.99903	14.008
1.55284	4.16076	14.008
1.36579	3.65959	14.007
1.61939	4.33914	14.007
1.93795	5.19219	14.012
2.89057	7.74498	14.009
1.31405	3.52082	14.009
1.82091	4.87921	14.006
	Mean,	14.0085

Calculated with H = 1.0076, Cl = 35.4574, and Ag = 107.881. These values for Cl, Ag and N are obtained by combining the data given above with the ratios Ag : NO_3 and Ag : Cl as formerly determined in the Harvard Laboratory.

Iodine and Silver.—Baxter and Tilley[2] have determined the ratio between iodine pentoxide and silver. The pentoxide was first reduced, in solution, by hydrazine hydroxide, and the iodine was afterwards precipitated and weighed as silver iodide. Two series of determinations were made, one by Tilley, the other by Baxter. The results, with all corrections applied, were as follows:

SERIES I.

Weight I_2O_5.	Silver used.	Ratio.
6.06570 9.48035[3]	3.92027 6.12611	0.646234
7.73052	4.99564	0.646223
12.63909	8.16777	0.646231
9.49913	6.13841	0.646208
8.34369	5.39202	0.646239
8.83155	5.70715	0.646223
6.77487	4.37803	0.646216
	Mean,	0.646225

---

[1] This Journal, 31, 6. The actual analyses were all made by Tiede. Richards is only responsible for the methods employed in the work.

[2] This Journal, 31, 201.

[3] The first two solutions were inadvertently mixed, and hence are combined here.

SERIES II.

Weight I_2O_5.	Silver used.	Ratio.
12.09036	7.81320	0.646234
6.29744	4.06957	0.646226
10.89880	7.04309	0.646226
9.33895	6.03505	0.646222
10.15370	6.56160	0.646236
11.00453	7.11141	0.646226
7.01649	4.53431	0.646236
9.33573	6.03304	0.646231
8.72163	5 63619	0.646231
9.01524	5.82591	0.646229
	Mean,	0.646230

Combining these figures with the former determinations by Baxter of the silver-iodine ratio, the authors find, with reference to O = 16, Ag = 107.850 and I = 126.891.

Carbon.—Scott[1] has sought to determine the atomic weight of carbon by means of analyses of tetraethylammonium bromide, $C_8H_{20}NBr$. This salt was titrated against silver solutions, and the ratio so determined gave the subjoined molecular weights, when Ag = 107.93.

Weight bromide.	Weight Ag.	Mol. wt bromide.
5.07039	2.60146	210.360
5.26380	2.70142	210.305
7.10662	3.64683	210.325
6.79951	3.48976	210.293
2.72225	1.39695	210.330
6.24530	3.20481	210.326
5.74581	2.94853	210.323
5.21663	2.67699	210.321

From these figures, when NH_4Br = 97.995 and H = 1.0075, C = 12.026, a very high value. One experiment was also made with the corresponding methyl compound, of which 8.64585 grams balanced 6.05348 grams of silver. Hence, C = 12.024. With Ag = 107.88 the values become C = 12.019 and 12.017. All weights were reduced to a vacuum.

In a criticism of Scott's work, Thorpe[2] has pointed out the possibility of errors due to the vacuum reductions, errors discussed long ago by Marignac, and recently, in more detail, by Guye and Zachariades.[3] The substances analyzed were weighed in powder, under which conditions they are liable to condense and occlude air. A probable correction, applied to Scott's weighings, reduced the atomic weight of carbon to 12.008, in harmony with other good determinations. To this criticism Scott[1] published a rejoinder, seeking to show, on the basis of experimental evidence, that the supposed errors do not, in fact, exist. According to Guye and Zachariades, the errors noted by them in the study of 26 compounds may amount to as much as, or even more than, 3 parts in 10,000.

---

[1] *J. Chem. Soc.*, 95, 1200.

[2] *Proc. Chem. Soc.*, 25, 285.

[3] *Compt. rend.*, 149, 593 and 1122.

The atomic weight of carbon has also been deduced by Baumé and Perrot[2] from density determinations of methane and ethane. For methane, the following weights of the normal liter are given:

0.71688	0.71633
0.71655	0.71670
0.71631	0.71676
0.71667	0.71723
0.71749	....

From the mean, 0.7168 gram, by different methods of reduction, the authors find values for C ranging from 12.003 to 12.005.

For the normal liter of ethane the following weights were found:

I.	II.
1.35671	1.35600
1 35679	1.35610
1 35671	1.35653
1.35652	1.35640
1.35700	1.35590
1.35640	1.35640

The mean of the second series, 1.3562 grams, is preferred by the authors. Reduced by Leduc's method of molecular volumes it gives C = 11.996. By Berthelot's method of limiting densities, C = 12.004. By reduction with the critical constants C = 12.036. The results from ethane are evidently not conclusive. From the vapor density of toluene, as measured by Ramsay and Steele, Leduc[3] deduces C = 12.003.

Scott,[4] in a preliminary note, gives, without details, the results of combustions of naphthalene and cinnamic acid. In six analyses, 17.6175 grams of naphthalene gave 60.5355 of CO_2. Hence, C = 11.999. In two analyses, 8.6153 grams of cinnamic acid gave 23.0413 of CO_2. Hence, 12.0015. The cause of the discrepancy between these figures and those from the alkylammonium bromides remains to be discovered.

Phosphorus.—Ter Gazarian[5] gives the following figures for the weight of a normal liter of phosphine, PH_3.

---

[1] *Proc. Chem. Soc.*, 25, 286.

[2] *J. chim. phys.*, 7, 369; also *Compt. rend.*, 148, 39.

[3] *Compt. rend.*, 148, 832. For other papers by Leduc on atomic weights and gaseous densities see *Compt. rend.*, 148, 42 and 548.

[4] *Proc. Chem. Soc.*, 25, 310.

[5] *Compt. rend.*, 148, 1397; *J. chim. phys.*, 7, 337.

1.52955
1.52907
1.52933
1.52944
1.52907
1.52933

From the mean, 1.5293 grams, he deduces the atomic weight P = 30.906, when H = 1.008. The value found is very low.

Vanadium.—Prandtl and Bleyer[1] have redetermined the atomic weight of vanadium by analyses of carefully purified vanadyl trichloride, $VOCl_3$. The substance, after weighing, was decomposed by water, in presence of a little zinc. The latter reduced the vanadium to its lower form of oxidation, and also prevented the escape of chlorine, either as free element or as oxides. In the filtrate from the solution the chlorine was determined as silver chloride. Two series are given, with vacuum weights, as follows:

I.

Weight $VOCl_3$.	Weight AgCl.	Ratio.
5.47218	13.54724	40.393
5.85234	14.50771	40.346
3.23175	8.00636	40.365
5.24732	13.01359	40.322
3.56589	8.83375	40.367

Hence, rejecting the first analysis, V = 51.133.

II.

Weight $VOCl_3$.	Weight AgCl.	Ratio.
4.91432	12.18494	40.331
3.64470	9.04685	40.287
4.96088	12.30438	40.318
6.46766	16.04292	40.315
4.33158	10.74624	40.308
4.05060	10.04498	40.325

Hence, V = 50.963. Mean of both series, 50.048, when Ag = 107.88 and Cl = 35.46.

Arsenic.—Baxter and Coffin,[2] by analyses of silver arsenate, have redetermined the atomic weight of arsenic. Two essentially distinct methods were employed. First, the arsenate was heated in gaseous hydrochloric acid, and so converted into silver chloride. Secondly, the arsenate was dissolved in nitric acid, and the silver was then precipitated, with the usual precautions, either as chloride or as bromide. Six series of results are given, which, with all corrections applied, are as follows:

---

[1] *Z. anorg. Chem.*, 65, 152.

[2] This Journal, 31, 297.

I —FIRST METHOD

Weight arsenate	Weight AgCl	Ratio
3 17276	2 94922	0 929544
2 65042	2 46367	0 929539
3 51128	3 26396	0 929564
5 83614	5 42503	0 929558
5 72252	5 31947	0 929568

II —SECOND METHOD

4 59149	4 26796	0 929537
3 38270	3 14436	0 929542
	Mean, Series I and II,	0 929550

III —SECOND METHOD

Weight arsenate	Weight AgBr	Ratio
8 75751	10 66553	1 21787
6 76988	8 24545	1 21796
5 19424	6 32590	1 21787
5 33914	6 50258	1 21791
8 24054	10 03552	1 21782
7 57962	9 23147	1 21793
6 05230	7 37106	1 21789

IV —FIRST METHOD

Weight arsenate	Weight AgCl	Ratio
4 67268	4 34389	0 929636
7 71882	7 17597	0 929672
5 28049	4 90908	0 929664
4 25346	3 95424	0 929652
3 47340	3 22893	0 929616
5 17269	4 80879	0 929650
4 10766	3 81858	0 929624

V —SECOND METHOD.

5 47133	5 08643	0 929652
	Mean, Series IV and V,	0 929646

VI.—SECOND METHOD

Weight arsenate.	Weight AgBr	Ratio
4.96261	6 04440	1 217988
5 31743	6 47658	1 217991
4.46882	5 44300	1 217995
4 16702	5 07539	1 217990

Series I, II and III are in close agreement, and Series IV, V and VI agree also; but the two groups differ, because of differences in the samples of arsenate employed. The first group is preferred, and gives, in mean, when Ag = 107.88, As = 74.957.

Chromium.—Two memoirs upon the atomic weight of chromium have been issued from the Harvard Laboratory. Baxter, Mueller and Hines[1] analyzed pure silver chromate, by dissolving the salt in dilute nitric acid, and after reducing the chromium to the chromic state, either by sulphur dioxide or by hydrazine sulphate, precipitating the silver as chloride or bromide. Two series of results are given, as follows; with all corrections applied.

---

[1] This Journal, 31, 529.

I.—CHLORIDE SERIES.

Weight chromate.	Weight AgCl.	Ratio.
10.30985	8.90908	0.864132
8.26920	7.14492	0.864040
6.56679	5.67444	0.864111
	Mean,	0.864094

II.—BROMIDE SERIES.

Weight chromate.	Weight AgBr.	Ratio.
2.63788	2.98621	1.13205
2.82753	3.20084	1.13203
2.33454	2.64268	1.13199
1.77910	2.01402	1.13204
2.33198	2.63994	1.13206
3.10402	3.51390	1.13205
2.92751	3.31427	1.13211
4.21999	4.77762	1.13214
5.24815	5.94104	1.13203
6.24014	7.06484	1.13216
7.923-3	8.96982	1.13211
	Mean,	1.13207

Using the silver-chlorine ratio of Richards and Wells, and the silver-bromine ratio of Baxter, these determinations give 65.0333 as the percentage of silver in Ag_2CrO_4. Hence, if Ag = 107.88, Cr = 52.008.

The second memoir, by Baxter and Jesse,[1] relates to analyses of silver dichromate, by essentially the same methods as those used in the previous investigation. The corrected results are subjoined.

Weight dichromate.	Weight AgBr.	Ratio.
5.71554	4.97149	0.869820
4.87301	4.23888	0.869869
7.45476	6.48425	0.869813
4.75269	4.13420	0.869865
8.15615	7.09495	0.869890
6.15412	5.35309	0.869839
6.83662	5.94678	0.869842
5.39883	4.69631	0.869876

In a single experiment, 6.26657 grams of the dichromate gave 4.16076 of silver chloride. From all of the data, the percentage of silver in $Ag_2Cr_2O_7$ is 49.9692. Hence, with Ag = 107.88, Cr = 52.013. The rounded-off value 52.01 is adopted.

Tellurium.—A new method for detaining the atomic weight of tellurium has been adopted by Lenher.[1] The double bromide, K_2TeBr_6, was converted into KCl by first heating in chlorine, and afterwards in gaseous hydrochloric acid. The determinations were made with tellurium from three widely different sources, and calculated with Cl = 35.46, Br = 79.92, and K = 39.095. All weights were reduced to a vacuum. The results obtained, in three series, were as follows:

---

[1] THIS JOURNAL, 31, 541.

Weight K_2TeBr_6.	Weight KCl	At. wt. Te.
	I.	
2.33360	0.50779	127.54
1.27372	0.27716	127.54
1.47573	0.32111	127.56
1.65715	0.36059	127.55
1.54006	0.33513	127.5
	II.	
1 82810	0.39778	127.56
1 87342	0.40765	127.55
1.48045	0.32214	127.55
2.24775	0.48911	127 54
	III.	
Weight K_2TeBr_6.	Weight KCl.	At wt. Te.
2 37899	0.51767	127.54
1 79926	0.39146	127.64
0 94102	0.20476	127 56
1.55357	0.33806	127.54
1 95038	0.42440	127.54
1 73248	0.37698	127.5
1 81923	0.39586	127.55

Mean of all as one series, Te = 127.55.

Lenher's researches, like those of several previous investigators, have had in view the determination of the homogeneity of tellurium, a conclusion which seemed to be finally established. Browning and Flint,[2] however, by a special process of fractionation, believe that they have strong evidence in favor of the view that tellurium is complex. When tellurium tetrachloride is decomposed by water, part of the tellurium is precipitated as TeO_2 and part remains in solution, to be recovered by subsequent treatment with ammonia and acetic acid. These two portions, converted into basic nitrate of tellurium, gave different values for the atomic weight of the element. From the first precipitate, Te = 126.49 in mean, and from the second Te = 128.85. The investigation is to be continued.

Mercury.—Preliminary determinations of the atomic weight of mercury have been published by Easley.[3] First, mercuric chloride was reduced by a well-known reaction with hydrogen peroxide. The mercury was collected mainly in a globule, but a small part of it which remained disseminated, was redissolved and determined electrolytically. With vacuum reduction the results obtained were as follows:

---

[1] THIS JOURNAL, 31, 20; see also discussion by Hinrichs, *Compt. rend.*, 148, 484.

[2] *Am. J. Sci.*, [4] 28, 347.

[3] THIS JOURNAL, 31, 1207.

Weight $HgCl_2$.	Weight Hg.	At wt Hg
23.43239	17.30826	200.44
12.59751	9.30608	200.52
10.94042	8.08134	200.46
11 73734	8.67044	200.50
	Mean,	200 48

Secondly, mercury was removed from the chloride as in the preceding experiments, and the chlorine in the filtrate was precipitated and weighed as silver chloride, with all the known precautions. The corrected data are as follows:

Weight $HgCl_2$	Weight AgCl	At wt. Hg.
10.50276	11 08744	200.64
9.03634	9.54027	200.62
23.43239	24.73606	200 65
10.94042	11 55158	200 59
11 11409	11 73470	200 60
16.63910	17.56808	200 60
	Mean,	200.62

Calculated with Ag = 107.88 and Cl = 35.46. Easley regards the second series as the more trustworthy. The investigation is to be continued by other methods.

Rhodium.—Two inaugural dissertations on the atomic weight of rhodium have appeared from Gutbier's laboratory at Erlangen. Renz reduced the rhodium pentamine bromide, $Rh(NH_3)_5Br_3$, in hydrogen, and cooled the remaining metal in an atmosphere of carbon dioxide. With H = 1.008, N = 14.01, and Br = 79.92 and vacuum weights, the subjoined results were obtained.

Weight bromide.	Weight Rh.	At wt Rh.
0.87624	0.21057	102.784
1.56500	0.37638	102.980
2.04033	0.49069	102.888
2.00120	0.48135	102.908
1.89278	0.45525	102.901
2.30210	0.55416	103.014
1.02065	0 24555	102.937
1.31485	0.31622	102.890
1.86060	0.44766	102.947
1.51040	0.36339	102.942
	Mean,	102.919

H. Dittmar's dissertation deals with the corresponding chloride,

$Rh(NH_3)_6Cl_3$, by essentially the same method as that of Renz. With vacuum weights and Cl = 35.46, the following results are given:[1]

Weight chloride	Weight Rh.	At. wt Rh
2.01526	0.70465	102.987
1.83589	0.64173	102.937
1.57210	0.54934	102.884
2.17528	0.76046	102.955
2.03911	0.71271	102.925
2.20000	0.76890	102.916
1.02840	0.35941	102.908
	Mean,	102.930

Palladium.—Gutbier, Haas and Gebhardt[2] have redetermined the atomic weight of palladium by analyses of palladosamine bromide, $PdN_2H_6Br_2$. Two series of reductions in hydrogen are given, with vacuum weights, and H = 1.008, N = 14.01, and Br = 79.92 for the antecedent value.

I

Weight bromide	Weight Pd	At. wt. Pd.
0.54402	0.19286	106.495
0.80237	0.28468	106.630
2.06470	0.73274	106.673
2.64770	0.93978	106.697
1.73455	0.61563	106.688
0.91601	0.32509	106.676
1.29106	0.45821	106.682
2.26758	0.80490	106.705
1.77729	0.63082	106.693
1.90770	0.67704	106.677
3.09278	1.09783	106.708
1.98039	0.70288	106.692

II.

Weight bromide	Weight Pd.	At. wt. Pd.
0.42942	0.15228	106.546
0.76884	0.27271	106.586
3.32461	1.17987	106.673
0.62795	0.22270	106.559
2.68383	0.95245	106.670
1.40117	0.49731	106.689
2.61673	0.92877	106.694
2.64229	0.93787	106.699
2.54424	0.90293	106.674
2.00456	0.71143	106.680
1.50032	0.53253	106.698
2.84500	1.00992	106.715

---

[1] Dittmar's work has also appeared in *Sitzungsb. phys. Med. Soz. Erlangen*, 40, 184.

[2] *J. prakt. Chem.*, [2] 79, 457. This includes the thesis work of Haas cited in my 1908 report. Gutbier has also published the thesis work of Krell and Woernle, *J. prakt. Chem.*, 79, 235. The data are already given in previous reports of this committee.

The authors reject some of the determinations, and conclude that Pd = 106.689 is the most probable value.

Iridium.—In a preliminary notice presented to the British Association for the Advancement of Science, Archibald[1] states that analyses of potassium chloroiridate give the atomic weight Ir = 192.90. The investigation is not completed, and no details are published.

Platinum.—A very elaborate memoir on the atomic weight of platinum is also due to Archibald.[2] The chloroplatinates and bromoplatinates of potassium and ammonium were analyzed, with all known precautions, and many ratios were so determined. The platinum itself was weighed, and also the silver and silver halide corresponding to the halogens in the several salts. In the analyses of the potassium compound the chlorine or bromine determinations were made in two portions, giving the halogen corresponding to the platinum, that is, the part lost on ignition in hydrogen, or four atoms, and that belonging to the potassium, two atoms.

The actual data relative to the weighings, and the individual determinations of atomic weight, are unfortunately too voluminous to be reproduced here. The mean results given by the various ratios are as follows:

FROM K_2PtCl_6 (14 ANALYSES).

Ratio	$K_2Cl_6 : Pt$	Pt = 195.23
"	$4AgCl : Pt$	195.21
"	$2AgCl : Pt$	195.24
"	$4AgCl : K_2PtCl_6$	195.20
"	$2AgCl : K_2PtCl_6$	195.24
"	$4Ag : Pt$	195.22
"	$2Ag : Pt$	195.23
"	$4Ag : K_2PtCl_6$	195.19
"	$2Ag : K_2PtCl_6$	195.22

FROM $(NH_4)_2PtCl_6$ (5 ANALYSES).

Ratio	$(NH_4)_2PtCl_6 : Pt$	Pt = 195.21
"	$6AgCl : Pt$	195.22
"	$6AgCl : (NH_4)_2PtCl_6$	195.23
"	$6Ag : Pt$	195.22
"	$6Ag : (NH_4)_2PtCl_6$	195.24

FROM $(NH_4)_2PtBr_6$ (3 ANALYSES).

Ratio	$(NH_4)_2PtBr_6 : Pt$	Pt = 195.25
"	$6AgBr : Pt$	195.22
"	$6AgBr : (NH_4)_2PtBr_6$	195.23
"	$6Ag : Pt$	195.21
"	$6Ag : (NH_4)_2PtBr_6$	195.22

FROM K_2PtBr_6 (6 ANALYSES).

Ratio	$K_2Br_6 : Pt$	Pt = 195.21
"	$4AgBr : Pt$	195.23

---

[1] *Chem. News*, 100, 150.

[2] *Proc. Roy. Soc. Edinburgh*, 29, 721.

Ratio $2AgBr : Pt$	Pt = 195.22
" $4AgBr : K_2PtBr_6$	195.21
" $2AgBr : K_2PtBr_6$	195.22
" $4Ag : Pt$	195.22
" $2Ag : Pt$	195.23
" $4Ag : K_2PtBr_6$	195.20
" $2Ag : K_2PtBr_6$	195.20

The arithmetical mean of these 28 ratios gives Pt = 195.22. Archibald, however, prefers to reject those which involve the weights of the original salts, using only 12 ratios. Mean, Pt = 195.23. This work evidently supplants all previous work on the atomic weight of platinum.

Radium.—From relationships between the wave-lengths of the spectral lines Watts[1] finds Ra = 226.56. Other atomic weights computed with that of radium are Mg, 24.32; Ca, 40.08; Sr, 87.62; and Ba, 137.41.

For the gaseous emanation of radium, by studying its physical properties, Gray and Ramsay[2] find a probable atomic weight of Em = 176. This conclusion, however, is not a finality.

Miscellaneous Notes.—Guye and Tsakalotos[3] have studied the determination of water of crystallization as a means of determining atomic weights. The substance investigated was barium chloride, but the results obtained, regarded as atomic weight determinations, were not satisfactory. Guye[4] has also discussed the variations from the law of Avogadro, and in another paper,[5] the general subject of atomic weight determinations by physical methods. A revision of the atomic weights of the rare earth metals is due to Urbain.[6] In a series of papers, not yet completed, Dubreuil[7] has undertaken to recalculate, by a peculiar mathematical method, the atomic weight determinations of Stas.

Mathematical relations between the atomic weights have been studied by Bernoulli,[8] Delaunay and Garnier,[9] Egerton,[10] Loring,[11] and Moir.[12] Hinrichs has also published a summary of his views regarding atomic weights,[13] and also several papers upon his method of calculation.[14]

---

[1] *Phil. Mag.*, [6] 18, 411.
[2] *J. Chem. Soc.*, 95, 1073.
[3] *J. chim. phys.*, 7, 215.
[4] *Ibid.*, 6, 769.
[5] *Arch. sci. phys. nat.*, [4] 22, 557.
[6] *Bull. soc. chim.*, [4] 5, 133.
[7] *Ibid.*, [4] 5, 260, 313, 341, 348, 610, 660, 708, 715, 852, 860, 1049, 1053, 1055.
[8] *Z. physik. Chem.*, 65, 391.
[9] *Chem. Zentr.*, [1] 615 (1909).
[10] *J. Chem. Soc.*, 95, 238.
[11] *Chem. News*, 99, 148; 100, 281.
[12] *J. Chem. Soc.*, 95, 1752.
[13] *Electrochem. Met. Ind.*, 7, 317.
[14] *Moniteur Sci.*, [4] 23, 731. *Compt. rend.*, 148, 1760; 149, 1074.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE HEATS OF COMBUSTION OF THE OCTANES AND XYLENES.

BY THEODORE WILLIAM RICHARDS AND RICHARD HENRY JESSE, JR

Received January 10, 1910.

Julius Thomsen sought, long ago, to obtain clues concerning the constitution of organic substances from the comparison of their heats of combustion. This endeavor, although it failed of a wholly satisfactory outcome, nevertheless showed certain relationships between the several members of homologous series and unmistakable differences due to variations in structure. Enough regularity is manifested in these results to show that the idea is worthy of further study.

The first step is obviously to seek among the older results for possible causes of the incompleteness in the relationships. This may be due either to the inadequacy of the theory or to the imperfection of the experiments. Turning to the first, one must admit at once that the heat of formation does not exactly represent the free energy of the change involved in the building up of the substance from other constituent elements; and therefore that it cannot represent the work which may actually be done by the chemical affinity. Yet nevertheless because in most cases where aqueous solutions are not concerned, free energy change is not very far from total energy change, a close relationship would be expected; moreover not only the free energy but also the bound energy must be supposed to have some relation to chemical structure. Hence if each of its constituents has a precisely regulated magnitude, the total energy change itself should be significant, although its significance might not be so easy to interpret as if it were simpler in its nature.

On the other hand, the experimental part of Thomsen's investigations was, as is well known, not wholly satisfactory and was undoubtedly inadequate in many cases. His universal burner gave too high results with all liquids having boiling points much above room temperatures, and the higher the boiling point the greater was the error. On the other hand, the results of Berthelot and Stohmann were probably too low in the cases of the more volatile liquids, because in these cases some of the liquids undoubtedly failed to burn. Hence, without further light upon the subject, one would be inclined to give more weight to Thomsen's figures with the lower-boiling substances and to shift the weight gradually over to Berthelot's and Stohmann's, as the boiling point rises. Compromises of this sort, however, cannot but be unsatisfactory; and the facts point clearly toward the need of further experimental work free from the inaccuracies of that now available. The precision needed is indeed of a high order, for differences of structure often cause but slight variations in the total magnitude of the heat of combustion of the substances; and upon these slight variations the inference wholly depends.

For example, it will be seen later that the greatest deviation between the heats of combustion of various octanes is no greater than one-third of one per cent. and if the magnitude of the variation is to be certain within one-tenth of its value, the several observations must be determined to within less than two one-hundredths of one per cent., a degree of precision which has never been approached in thermochemical work of this kind.

It was with the hope of obtaining more precise knowledge of these important quantities that E. Fischer and Wrede,[1] in Berlin, and Richards, Henderson and Frevert, in Cambridge, began the revision of thermochemical data, using quite different methods, which seem to give about equally reliable results. The German experimenters used the electrical resistance thermometer and comparatively small temperature changes, applying the usual correction for cooling. On the other hand, the American experimenters contented themselves with good mercury thermometers and arranged the conditions so that these thermometers could be read with precision and could yield sufficiently accurate results, eliminating the cooling correction by causing the environment of the calorimeter to change in temperature at the same rate as the inner vessel itself. Both groups of experimenters have attempted only to determine a comparatively small number of a few typical substances. The work of revising the data is therefore only at its very beginning.

The present research consists of a continuation of the earlier Cambridge work. The method used in that work was chosen for the continuation because it is much more speedy in execution than that used in Germany. The electrical thermometer, admirable as it is in many respects, is an exceedingly complicated instrument, and the calculation of a single temperature from the observed data requires much patience. The complete calculation of a single calorimetric determination by this method requires several hours. This is in addition to the laborious preparation, and adjustment of the sensitive electrical instrument. On the other hand, the adiabatic Harvard method is simple in the extreme. The temperature change is read off from the thermometers at once and the only corrections which have to be applied are those easily calculated figures which give the error of the mercury thermometer at each reading. The correction for cooling is non-existent. Hence it is easily possible for a single experimenter by the Harvard method to conduct and calculate three determinations in a single day, whereas it would hardly be possible for him to do more than one a day by the more elaborate method. If this more elaborate method yielded more accurate results, the difference in time ought not seriously to influence the experimenter, but because apparently the range of error is about the same in both cases, the advantage of the quicker method is very obvious.

---

[1] Fischer and Wrede, *Kgl. Preuse, Acad. Sitzber.*, 19, 20, 21, 687 (1904). An important correction of the detail is to be found in *Z. physik. Chem.*, 53, 161 (1903).

The object of the research and the method of attack having thus been clearly outlined, it becomes necessary to justify the selection of the individual substances to be chosen for experimentation. Obviously the compounds should be complex enough to allow of considerable differences in structure and yet, on the other hand, not so complex as to complicate too greatly the interpretation of the results. The theoretical problem is greatly simplified by avoiding the presence of more than two elements Moreover the compounds should be capable of being prepared in a state of very great purity, free from other substances which could seriously influence their heats of combustion. Among the incalculable number of organic compounds, these deciding criteria narrow greatly the range of choice; and from the theoretical point of view there seemed to be no question that the simpler hydrocarbons are the compounds most suitable to serve as a starting point Among these the octanes seemed to be, on the whole, the best, because their molecular complexity is enough to allow of great variety of arrangement, but not so great as to confuse the relationships. The difficulty of obtaining them in a pure state seemed in the first place to be a serious barrier, but Dr. Latham Clarke, during the summer of 1906, kindly undertook the working out of methods for this purpose. He became greatly interested in the problem from the point of view of organic synthesis and was able, in the course of several years, to prepare larger quantities than had ever been made before of these hydrocarbons and of great purity. Most of those which he prepared had indeed never been isolated by previous experimenters. It is our hope that in the course of time all of the isomeric octanes may be prepared and investigated. The present paper contains results for only five, the others having not yet been prepared in sufficient quantities for calorimetric experiments.

In order to refer the determinations to a satisfactory and perfectly definite standard, under the somewhat new conditions involved in this new series of experiments, it was desirable to repeat the determinations made with sugar and benzene by Richards, Henderson and Frevert, in the research already mentioned. These two substances serve admirably for calorimetric standards because they are so easily obtained in a pure state. They typify respectively the solid and the volatile liquid; methods which will serve for these two substances can easily be made to serve for most others among the combustible organic substances. As will be seen, the value obtained by the earlier experimenters for sugar was confirmed, and the anomalies in the combustion of benzene have been explained and corrected so that for this substance yet more satisfactory results are to be chronicled than were reported in the earlier paper.

The investigation showed that not only must the substance be confined in flexible glass bulbs, but that special pains must be taken with regard to the form of the containing capsule and the details of manipulation in order to insure complete burning. When the proper conditions have been established, the presence of nitrogen in the compressed gas of the bomb does not prevent the complete combustion of the hydrocarbon. It will be seen that the results finally obtained showed a very satisfactory agreement among themselves. Without the high degree of precision made possible by the devices to be described, the data could not have been accurate enough to form the basis of any important conclusions; because, as has been said, the variations from which inferences must be drawn are small in proportion to the total magnitude to be measured.

Apparatus.

During the first part of the work the adiabatic calorimeter was essentially like that used by Richards, Henderson and Frevert.[1] It consisted of a large silver calorimeter holding about 4 4 liters, in which was immersed the calorimetric bomb. This was surrounded below and on all sides by a jacketed vessel and covered with a copper pan. Both of these receptacles contained alkali to which acid was added in order that the temperature of the surroundings of the calorimeter should keep pace with that of the calorimeter itself. The temperature of this solution was easily and quickly changed. The air space between the silver calorimeter and the copper jacket was made as small as possible, the two vessels being insulated thermally from one another by pieces of cork. The complete insulation was tested electrically just before each experiment. The first diagram (Fig. 1), taken from the earlier paper, depicts the arrangement in section.

The method of carrying out the determinations was so nearly similar to those described in the earlier paper that details are unnecessary. In one essential point, however, an alteration was introduced, namely as to the rate of stirring. On account of the experience recently gained in other thermochemical work in the laboratory (namely that carried out by Dr. L. L. Burgess and one of us concerning the heat of solution of metals),[2] the agitation of the liquid in the calorimeter was more thorough than in the earlier experiments. On this account a correction had to be determined and applied for the heat gained through friction. This correction will be discussed later.

In the later experiments the method of jacketing the calorimeter was modified in a fashion which greatly increased the convenience of experimentation. It may be remembered that Richards and Forbes[3] made calorimetric determinations of the heat of amalgamation of metals in a

---

[1] *Proc. Am. Acad.*, [illegible] 573 (1907); *Z. physik. Chem.*, 59, 532 (1907).

[2] In press—several

rnagie Inst., No. 56.

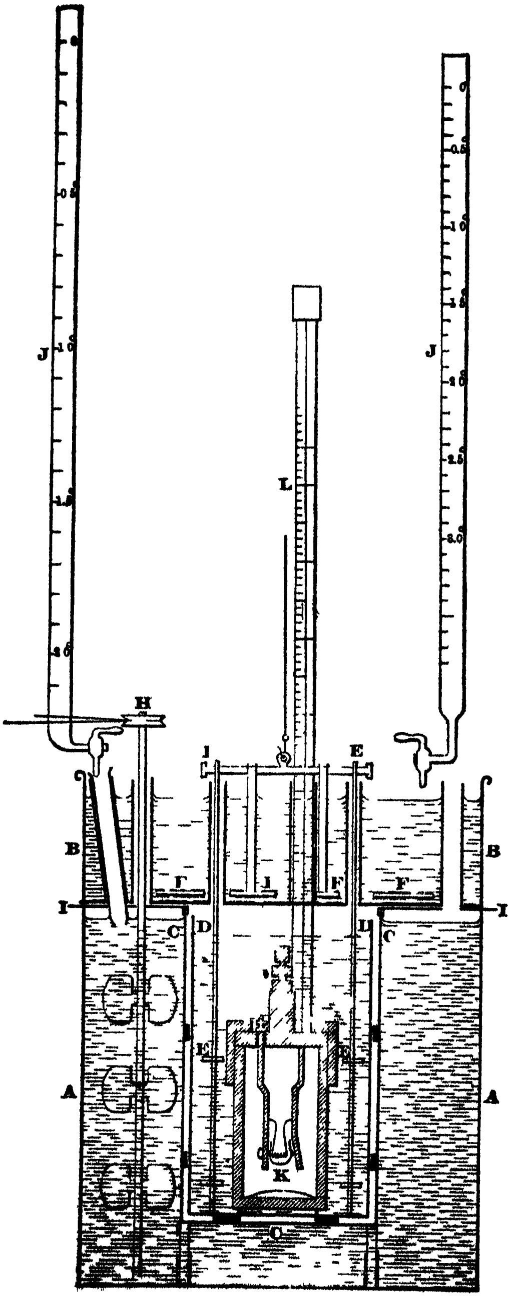


Fig. 1.

A. Outer vessel. B Covering vessel C Nickel-plated copper can D[illegible]
[illegible] for calorimeter E Stirrer for covering vessel F Stirrer fo[illegible]

calorimeter wholly enclosed in a single jacketing vessel, which was immersed below the surface of the liquid in the outer vessel Dr. F. Wrede suggested the extension of the use of this kind of calorimeter for the bomb also The obvious advantage of having only one jacketing vessel to regulate in temperature was found practically to outweigh the difficulty in keeping the apparatus water-tight. We succeeded in arranging the other experimental details so that this method of completely immersing the can surrounding the calorimeter will always be used in the future, in preference to the older apparatus involving a separate lower vessel and a movable pan above The second diagram (Fig 2) represents the arrangement.

A brief description of the essential features of the new apparatus is in place. To the top of the inner copper can C was soldered a flat projecting flange of copper of the same thickness as the can itself, and to the under edge of this flange was soldered a ring made from rectangular brass rod 1/8 inch thick ar[illegible] inch high. As may b[illegible] figure, this r[illegible] from the s[illegible] ear[illegible] any possible thermal lag of the heavier mass of metal does not affect the inner vessel. The cover to this can consisted of a circular piece of sheet copper bearing tubes for the thermometer and stirrer and having on its upper edge a brass ring similar to the one soldered beneath the flange. When the calorimeter and its contents had been placed in the vessel (C), the cover was put on and a gasket of black sheet rubber was placed between the flange and the edge of the cover. These were then clamped together by means of several small brass clamps, sealing the can perfectly water-

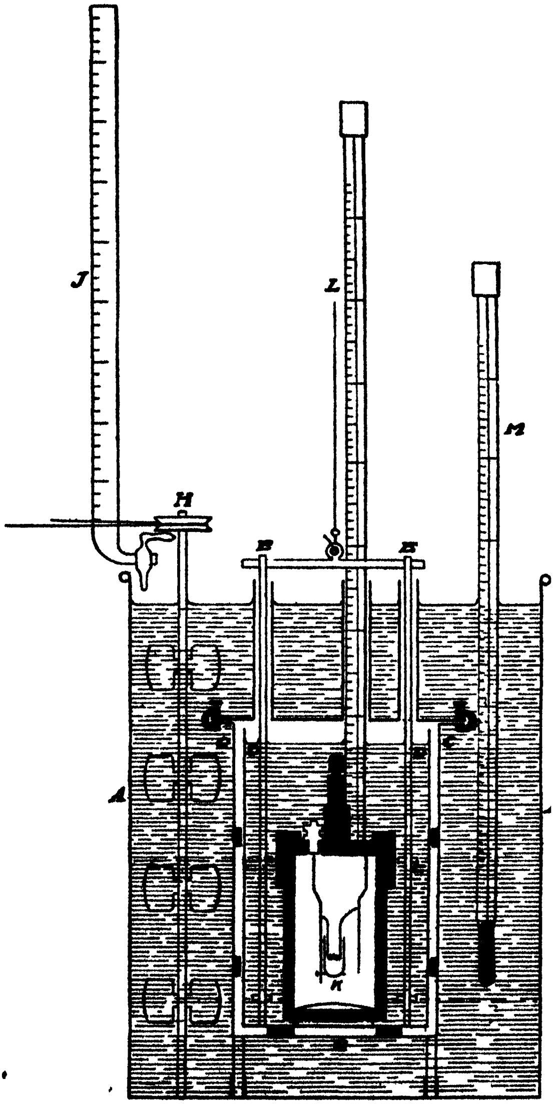


Fig 2
Vertical Section

A Outer vessel
C Nickel-plated copper can.
D Silver calorimeter
E Stirrer for calorimeter
H Stirrer for outer vessel
J Burette
K Crucible containing substance to be burned
L Thermometer for calorimeter
M Thermometer for outer vessel

tight. The whole arrangement was then completely submerged in the alkaline liquid in the outer vessel. With this arrangement one burette only is necessary, and only two thermometers must be compared. Determinations on sugar with this apparatus gave results identical with those obtained by the use of the older apparatus; that is to say, the advantage of this new form consists not so much in increased accuracy as in greater ease of operation.[1]

For accurate work the temperature of the outer jacket must be kept within 0 1° of that in the calorimeter. In following the rise, the acid was introduced in the immediate neighborhood of a rotary triple propeller driven by an electric motor at the rate of about 250 revolutions a minute. In this way equilibrium was established throughout the whole outer bath within a few seconds after the introduction of a quantity of acid. The sulphuric acid was run into the outer jacket (and into the cover also, in the earlier experiments) from the burettes graduated in terms of the volume of acid necessary to raise the vessels and their content 0.1°. The temperatures were observed at the same time by the thermometers.

As may readily be seen from the above description, the operator of the earlier form of apparatus was compelled at the same time to manipulate two burettes and to read the three thermometers in the calorimeter, the outer vessel and the cover. Since there was generally a rise of about 2° in the two minutes following the combustion, this requires rapid reading and manipulation; nevertheless, after some experience has been acquired, the task is not nearly so difficult as might at first sight be supposed. The second form of apparatus, in which the calorimeter was wholly beneath the solution in the larger vessel, does away with one burette and one thermometer.

The inner vessel (C) which held the calorimeter proper was in each case a can of heavy copper, nickel-plated and well burnished on the inside. Its walls were about of the same thickness as those of the silver calorimeter, so that the lag in heating each might be approximately the same. It was supported by metallic legs 5 centimeters high, so that there was plenty of room for the circulation of the alkaline solution beneath it.

The calorimeter itself (D) was a can of spun silver, 1357 g. in weight and of 4432 cc. capacity. It was placed within the can (C) and was insulated from it by pieces of cork. In the older form of apparatus, the air space between the silver and the nickel surface was about 3 millimeters thick; in the later form it was about 5 millimeters thick. The complete insulation was tested electrically before each calorimetric experiment.

---

[1] Of the experiments recorded in this paper, those marked experiments 7–11 and 30–45, inclusive, were made with this "submarine" form of apparatus; all the others were made with the older form.

The bomb was the one used by Richards, Henderson and Frevert. It was of the Atwater type, made by Singleton and Dinsmore, Middletown, Connecticut.[1] The inside of the bomb and the bottom of the cover were lined with spun platinum. To prevent possible heat effects from the oxidation of the lead gasket (used for sealing the bomb) during combustion, Richards, Henderson and Frevert protected the gasket by means of strips of gold foil.[2] In the earlier stages of the present work also, this method was used, but the accurate fitting of the gold strips is a tedious task, and, moreover, when the task was completed, it was necessary to use great force to screw down the top of the bomb sufficiently to prevent leakage. It was finally found that heavily gold-plated gaskets would answer the purpose. The gaskets were given three coats of gold, each coat being well burnished before the next was applied. The coating was not enough wholly to prevent oxidation, but the amount oxidized in a single determination was not enough to affect the heat of combustion appreciably. This was shown by the fact that the results of determinations on sugar with the gaskets protected by gold foil agreed well within the experimental error with those made with the gold-plated gaskets.

Instead of the capsule generally used for holding the substance to be burned, platinum crucibles were substituted. At first a larger crucible weighing 16 grams was used, but later it was found desirable to substitute a smaller crucible weighing 6 grams. The differences in heat capacity caused by this and other slight changes in the system were duly considered in the calculation.

Two thermometers were used for this work, both of the Beckmann type, graduated to 0.01°. One had been made by Fuess, and had a bulb containing about 75 grams of mercury and a very wide thread. The other was from Goetze, and had a smaller bulb and a narrower thread. Both were carefully standardized by comparison with two Baudin thermometers which had been calibrated by the French Bureau des Poids et Mèsures. The thermometers were also compared with two other thermometers of the Beckmann type which had also been separately standardized against the Baudin thermometers. The agreement was excellent. The Fuess thermometer had been standardized by the German Physikalisch-Technische Reichsanstalt, and this verdict agreed with the comparison with the French thermometers. No difference in the results obtained by the two thermometers could be detected.

The thermometers were standardized and all the determinations were made in a room provided with such regulating devices that the temperature could be kept very constant. Therefore no corrections are necessary for effects of differences in room temperature on the projecting threads of the thermometers.

---

[1] Atwater and Snell, THIS JOURNAL, 25, 659 (1903).

[2] For details, see Richards, Henderson and Frevert, *Loc. cit.*, p. 576.

The oxygen used was supplied by the Linde Air Products Company, of Niagara Falls. It had been obtained from liquid air, and was free from carbon dioxide and from chlorine. Samples of each tank used were analyzed volumetrically for oxygen. The purity ranged in general from 97.5 per cent. to 98.2 per cent. of oxygen.

The Heat of Combustion of Sugar.

Two of the samples of sugar prepared for the work of Richards, Henderson and Frevert were still available for this work. These samples had been crystallized with all the necessary precautions: one (Sample A) from water, and the other (Sample B) from a mixture of water and ethyl alcohol of such proportions that the heat of combustion of the mixture was the same, gram for gram, as that of sugar itself. The concordance of the determinations on these two samples showed that not enough water was included in the crystals to be detected by thermochemical means.

The details of a combustion of sugar will serve to illustrate the method. The manipulation was similar except in a few minor points for the other substances burned.

About two grams of sugar in powdered form were weighed into the platinum crucible, and the crucible was placed on its support. This support consisted of a platinum ring attached to a heavy platinum wire projecting downward from the cover of the bomb and in metallic contact with it. Between this wire and a similar one, insulated from the bomb, was suspended a coil of fine iron wire, of measured length, the bottom of which just dipped into the sugar. If this wire is protected from the oxygen by being buried too deeply in the sugar, it is sometimes difficult to ignite the sugar by the passing of an electric current. In order to avoid a correction for the evaporation of water formed during the combustion, a little water, less than a cubic centimeter, was placed in the bomb. The cover was now placed on the bomb, and the latter was sealed by screwing down the steel cover-cap. In the earlier experiments, oxygen was run in until the gauge registered 35 atmospheres; later, as will be seen, a lower pressure was employed.

The water for the calorimeter was measured in a graduated flask, delivering a definite amount of water at 20°, and brought to the temperature at which it was desired to start the experiment. The alkaline solution in the jacket and the cover were adjusted to the same temperature. The bomb was placed in the calorimeter, and two insulated copper wires for the introduction of the electric current were attached to the platinum wires from which the fine iron coil was suspended. After the water had been poured into the calorimeter, the cover was put in place. The well-insulated electric connecting wires passed through the copper tubes in the cover provided for the wires of the calorimeter stirrer. When the thermometer and burettes were in place, the stirrers were started and the temperatures of calorimeter, jacket, and cover were equalized to within 0.01°. Readings were made every minute with the aid of a good hand lens, the thermometer being tapped by an electric vibrator immediately before each reading. When constancy had been obtained, the electric circuit was completed and the burning of the iron wire caused the combustion of the sugar. During the first rapid rise the temperatures of the outer vessels were kept from 0.05–0.1° higher than that of the calorimeter. This was done because the thermometer in the calorimeter had a slightly geater lag than that outside, and also in order to give time for the complete distribution of the heat in the jacket and cover. Richards and Burgess have shown that it is safer to keep the outer jacket a little too warm than a little too cold.[1] After the first two minutes the rise was very nearly complete and the temperatures were adjusted to within one or two hundredths of a degree. In five or six minutes the maximum temperature was reached, although readings were continued several minutes longer.

The stirring (at the rate of 68–74 strokes per minute) was much more energetic than in previous work, and caused a slight warming effect. In two blank trials of 30 and 40 minutes respectively the heating effect for 10 minutes was 0.0030° and 0.0033° with an average of 0.0031°. Thus, for experiments which lasted 7 or 8 minutes after the combustion was started, a correction of —0.002° was subtracted from the observed rise, and in those others which took 9 or 10 minutes the correction applied was —0.003°.

One centimeter of the iron wire weighed 0.00194 gram. The water equivalent of the system having been about 3760 grams, the rise due to the burning of 1 centimeter was calculated, from the heat of combustion of iron to the magnetic oxide, to be 0.0009°. Probably some ferric oxide forms also, augmenting this value slightly. The electrical heat needed to raise 1 centimeter of the wire to the point of combustion (perhaps 800°)[2] must have been enough to raise the calorimetric system through approximately an additional amount of about 0.00005°, so that the total amount to be subtracted from the thermometer reading for each centimeter of wire was approximately 0.001°, allowing for the small amount of electrical heat which must have been generated in other parts of the apparatus. This was verified by four experiments in which no sugar was burned, the combustion of the usual length of wire changing the temperature of the system 0.014°, 0.014°, 0.015°, and 0.015°, respectively, results very closely in agreement with the calculated value.

---

[1] *Loc. cit.*, in press.

[2] Fischer and Wrede assumed 600° as the temperature of ignition. *Z. physik. Chem.*, *Arrhenius Jubelband*, 69, 233 (1909).

After an experiment was ended and the gas had been allowed to escape, the interior of the bomb was carefully inspected for indications of incomplete combustion. No carbonaceous matter was found, except in a single preliminary experiment. This determination was, of course, rejected. No tests were made for carbon monoxide, since Richards, Henderson and Frevert found no traces of this gas upon repeated analyses.

A degree of acidity in the water in the bomb after combustion, capable of being neutralized by 4.0 cubic centimeters of a certain alkaline solution, indicated a quantity of nitric acid whose heat of formation must have raised the calorimeter 0.001°.[1] Corrections were duly made for this source of error.[2]

The following table records the results of a preliminary series of combustions. In these experiments the conditions were identical with those just detailed, the heat capacity being exactly the same, equivalent to about 3760 grams of water, and the same thermometer being used. Thus all the figures in the final column are comparable with one another and with the results of Richards, Henderson, and Frevert, where the same heat capacity was used, except for the fact that in the present case the weight of the sugar was reduced to the vacuum standard.

COMBUSTION OF SUGAR.

Preliminary Series.

Expt. No.	Weight sugar (in vacuum). Gram.	Observed rise of temperature (corrected for thermom. errors).	Correction for stirring.	Correction for iron wire burning.	Correction for HNO_3 formed.	Corrected rise due to sugar.	Corrected rise in temperature per gram sugar.
1	1.7577	1.868°	—0.002°	—0.015°	—0.003°	+1.848°	1.051°
2	2.0796	2.213	—0.002	—0.023	—0.004	+2.184	1.050
3	1.8473	1.964	—0.003	—0.015	—0.003	+1.943	1.052
4	1.9460	2.071	—0.003	—0.015	—0.004	+2.049	1.053
5	2.1769	2.306	—0.002	—0.015	—0.002	+2.287	1.050

The average rise of temperature in this calorimetric system for the combustion of 1 gram of sugar is thus 1.0512. For the same system, Richards, Henderson and Frevert found 1.0504 (or 1.0498, if allowance is made for the correction of the weight of sugar to vacuum, as has been done in the present calculation). The difference, about 0.13 per cent., is a small deviation, but one nevertheless greater than the probable accidental error of either average. A slight constant error is indicated; we are inclined to think that this may lie in the fact that in these later determinations the stirring of the calorimetric solution was far more rapid than in the earlier ones. The work of Richards and Burgess has shown that unless the agitation of the solution is so great that the rise of temperature of the solution is equably distributed throughout the whole calorimeter, a thermometer placed near the bottom of the calorimeter will register a temperature below the average value. Therefore the environment will not be kept warm enough, and some heat will be lost. The error thus caused is just about of the same magnitude indicated by the difference between the two series of experiments, and of course the later ones are far more trustworthy because this cause of uncertainty was removed. Incidentally it may be noted that this cause is by no means peculiar to the adiabatic method of calorimetry. It affects the cooling correction calculated by the Regnault-Pfaundler method quite as much as it affects the actual reading of the thermometer in the adiabatic method. Hence it is probable that in most calorimetric work the liquid has not been adequately stirred.

---

[1] The standardization of this solution was effected by the use of Thomsen's equation, $2N + 5O + H_2O + Aq = 2HNO_3Aq_3 + 29.8$ cal., assuming the heat capacity of the system to be equivalent to 3,760 grams of water.

[2] During the rise of about 2° enough water is evaporated to raise the aqueous pressure of the confined air space immediately above the surface of the water by 2 mm. of mercury. This causes a cooling effect in the neighborhood of 0.001°, an amount entirely negligible.

The proportions of water and metal in our calorimetric system were such that for temperatures between 0°–30° the decrease in the specific heat of water with rising temperature is about offset by the increase of the specific heat of the metal parts. Therefore there is little error in this respect in comparing the results of the present determinations done between 17.7–20.2° (at an average temperature of 19°) with those of Richards, Henderson, and Frevert, performed at an average temperature of 21.4°. Indeed it has been calculated with a good degree of approximation that the heat capacity of the system at 25° differed by less than 0.03 per cent. from that at 20°.

After the experience had been gained by the conduct of these preliminary determinations, liquids were studied, especially benzene and a number of esters. In the course of this work much further experience in calorimetry was gained, and in particular it was found that a smaller crucible was far more satisfactory than that of the large size. Accordingly, because sugar is a substance of great importance as a standard of reference, it was thought worth while to make another series with sugar, in which all the experience gained in the course of the work came into play. In this series of six determinations the heat capacity of the system had been somewhat less than in the preliminary experiments, because 10.5 grams of steel had been cut off the bomb in providing new holes to engage the spanner, 10 grams of platinum had been removed in substituting a smaller platinum crucible, and 9.2 grams less water were used in the calorimeter. The water equivalent of these changes amounted in all to 10.73 grams (which was 0.29 per cent. of the total water equivalent), and this system was used in the first two experiments recorded in the series given below. The other four involved a still somewhat smaller heat capacity, because in these last the pressure of the oxygen was only 20 atmospheres instead of 35 atmospheres. This change involves a further loss of water equivalent of 1.1 grams, or about 0.03 per cent. In the final column given below all the results are reduced to the same standard by adding 0.0003° to the figures in the last column obtained from Experiments 6 and 7 for 1 gram of sugar.

These two experiments just mentioned were made before the experiments with liquids, while Experiments 8 to 11 were made at the very conclusion of the whole research. The essential identity of the two sets is pleasing. Because of the close agreement of the results, the final figures in the last column are given to the fourth decimal place.

COMBUSTION OF SUGAR.

Final Series.

No. Exp.	Thermometer.	Weight of sugar.	Obs. rise of temperature.	Corr. for stirring and iron burnt.	Corr. for HNO_3.	Corr. temp. change	Temp. change for 1 gram sugar.	Temp. change for 1 g sugar corr. to lowest heat capacity.
6	B	1.5703	1.669°	—0.013°	—0.002°	1.654°	1.0533°	1.0536°
7	B	2.1784	2.312	—0.015	—0.002	2.295	1.0535	1.0538
8	B	2.0045	2.132	—0.016	—0.003	2.113	1.0541	1.0541
9	B	2.0563	2.187	—0.017	—0.002	2.168	1.0543	1.0543
10	B	2.0780	2.310	—0.017	—0.002	2.291	1.0539	1.0539
11	J	1.8772	1.997	—0.016	—0.003	1.978	1.0537	1.0537
								1.0539

Thus with the new heat capacity (0.32 per cent. less than in the previous series) the rise of temperature caused by 1 gram of sugar is 1.0539°, the extremes being less than 0.04 per cent. divergent from this mean. The preliminary series recalculated over to the basis of the new heat capacity would give 1.0545°, a value slightly greater, but probably within the limit of error of the first crude set of experiments where the individual determinations varied somewhat widely. It seems probable that the value 1.0539° is a correct one, and it may be used in subsequent work as the basis of conclusions concerning the relative heats of combustion with other substances as compared with sugar.

The Heat of Combustion of Benzene.

Two of the samples prepared for the previous work were still available.[1] These samples had been purified by several careful crystallizations: Sample A was from Merck's best grade of benzene and Sample B from Kahlbaum's "thiophenfrei" material. These had been preserved in well protected glass bottles with good ground-glass stoppers. Nevertheless, because they had been standing in this way for over two years it was thought best to prepare another specimen. Accordingly a new sample (C) was purified from Kahlbaum's "thiophenfrei" benzene by four successive crystallizations. In each case only about a third of the liquid was allowed to solidify. The crystals were allowed to drain slowly so that adhering mother liquor should be washed off by the liquid formed through the melting of the crystals themselves. In a determination conducted with all the ordinary precautions, no difference could be detected between the freezing point of the fourth crop of crystals and that of the mother liquor from which they had been crystallized. Furthermore, the temperature remained constant until practically all the liquid was frozen.

---

[1] *Proc. Am. Acad.*, 42, 578 (1907); *Z. physik. Chem.*, 59, 538 (1907).

It has been mentioned at the first of the paper that the earlier method of combustion was finally modified, and that a more trustworthy arrangement was made. Before describing the modifications it is worth while to record the results of new experiments with the use of the earlier method.

In brief, this old method was as follows: The benzene was sealed and weighed in a completely filled glass bulb with very thin walls. The bulb was placed in the platinum crucible within the bomb, on the top of a small weighed quantity of sugar, which was ignited as usual by the coil of iron wire. The burning of the sugar burst the bulb and inflamed the benzene. The remainder of the manipulation was precisely as described above in the case of cane sugar. The heat capacity was the same as that used in the earlier experiments, Nos. 1 to 5, with cane sugar, and the rate of stirring was the same. The following table contains the results of the combustion of benzene in this way, the larger crucible with a diameter at the top of about 35 centimeters having been used as the capsule for the combustion, and the oxygen containing about 5 per cent. of nitrogen.

COMBUSTION OF BENZENE.

Preliminary Series with Large Crucible.

No. of Exp.	Thermom.	Weight of benzene in vacuum. Gram.	Weight of sugar. Gram.	Correction for sugar burned.	Rise due to benzene	Rise per gram benzene.
12	B	0.7108	0.2715	0.286°	1.887°	2.655°
13	B	0.7535	0.2359	0.248	2.003	2.658+
14	B	0.6049	0.2711	0.285	1.607	2.657+
					Average,	2.657°

Thus 1 gram of benzene is shown to raise the calorimetric system 2.657°. Richards, Henderson and Frevert found for the combustion of benzene with oxygen containing the same amount of nitrogen the value 2.655°.[1] The difference of 0.002° is not much beyond the limit of error of the average and is just what one would have expected as a result of better mixing of the liquid in the calorimeter. Thus if the ratio of benzene to sugar 2.657/1.051 = 2.528, found by the new investigation, is compared with the older ratio 2.655/1.0504 = 2.528 (or, if the weights of benzene and sugar are both corrected to the vacuum standard, 2.526), the essential identity of the results is seen to indicate that the experimentation was really identical and to verify the previous work as far as accidental errors are concerned. The error due to the inadequate stirring in the older work was a constant one, and affected the experiments with sugar and with benzene in like manner, hence it is essentially eliminated from the ratio.

---

[1] *Proc. Amer. Acad.*, 42, 588 (1907).

It will be remembered, however, that the earlier experimenters found a higher result when the oxygen contained less nitrogen, showing that combustion with 5 per cent. of inert gas present had not been complete; and they were inclined to believe that even the highest value which they obtained, about 0.3 per cent. higher than the one just given, was not quite high enough. Pure oxygen was at that time not obtainable under this pressure, and the cause of the incomplete combustion was pointed out as a matter well worth further investigation. An important point in explaining the anomaly is the following fact demonstrated by repeated experience, namely that whenever the benzene vapor had a chance to become intimately mixed with the gases in the bomb before combustion took place (as for example, by the premature bursting of the glass bulb by the pressure of the oxygen), the combustion was always incomplete. Under these circumstances we have detected the odor sometimes of nitrobenzene and sometimes of phenol—substances which are notoriously hard to burn. Once after rinsing out the bomb and diluting the liquid as usual with sodium hydroxide, the solution turned yellow immediately before the color change in the phenolphthalein took place—a phenomenon which might have been due to the presence of paradinitrobenzene.

These observations clearly point to the inadequacy of the usual method of burning a volatile liquid absorbed in a mass of cellulose, because under these conditions some of the liquid inevitably evaporates prematurely. They also form an important step, as has been said, in the train of reasoning which guided us to a better result.

In the present work we have been fortunate enough to solve the difficulty and discover the cause of the incomplete combustion of the benzene as well as to show why this cause does not affect experiments with non-volatile substances, like sugar. We will show also that the suspicion that the true value is yet higher than the highest value found before was correct. The answer to the riddle was found only after protracted investigation. In the search for further light and experience, other liquids, especially methyl butyrate, methyl isobutyrate, and ethyl propionate, were subjected to calorimetric combustion, and it was through experience gained in working with these less combustible compounds that the error in the results of previous investigators with all volatile liquids became manifest. Therefore it may not be out of place here to describe the various methods which were tried in the attempt to obtain complete combustion of the esters.

At first the earlier method just described was used. This method was, however, obviously inadequate, for after the bomb was opened a distinct odor of the ester, varying in intensity in different experiments but always recognizable, could be detected in the issuing gases. Moreover, in several cases there was a deposit of carbon in the crucible. It seemed possible that the carbon was formed from sugar protected from the oxygen by the molten glass of the bulb, hence in a few experiments the bulb was placed on a small staging of heavy platinum above the surface of the sugar. In this way the sugar should have a chance to become thoroughly ignited before the melted glass could fall upon it. The plan succeeded, indeed, in eliminating the carbon, but the odor of ester was still very distinct. Evidently, at the moment when the bulb burst, some of the vapor was projected upward at a rate greater than the rate of propagation of the explosion; and as the amount which thus escaped was evidently insufficient to form an explosive mixture throughout the bomb, it escaped combustion.

The amount left unburned would naturally be greater, the greater the concentration of nitrogen present, for the effect of an inert gas in retarding the rate of propagation of an explosive wave is well known.[1] It is conceivable that the retarding effect here was so great that some of the vapor escaped combustion entirely. Dixon[2] has shown that in some cases an excess of one of the reacting gases also has a retarding effect, but this cause of incomplete combustion does not seem to have affected our work, probably because in no case the pressure of the oxygen exceeded 35 atmospheres.

These considerations adequately explained the effect of increasing the concentration of the nitrogen, and furnished the leading idea in effecting improvement.

The following arrangement was then tried. The bottom of the platinum crucible was so distorted as to form on one side a depression large enough to hold the bulb. On the bottom of the crucible, now somewhat above the bulb, sugar was piled in such a way that the capillary was buried in it. It was hoped that, when the bulb burst, the liquid would be projected into the burning sugar. Also, since the sugar was on a higher level, the vapor rising upward would have to pass through an area filled with flame. But here too there was evidence that part of the vapor escaped combustion.

---

[1] See Mellor, "Chemical Statics and Dynamics," pp. 466ff.

[2] *Phil. Trans.*, 184, 97 (1893). *J. Chem. Soc.*, 69, 774 (1896); 75, 631 (1899).

After a few fruitless experiments with an entirely different method, whereby it was hoped to reduce the rate of vaporization of the ester and thus to obtain a slower combustion, the use of the thin-walled bulbs was again resorted to The bulb was now placed in the bottom of a much narrower crucible. About half way up in this crucible and on top of the bulb was fixed a rectangular plate of thin perforated platinum foil, and sugar was put on top of this. By having this plate rectangular instead of disc-shaped, there was room for the passage of the vapor around the sides of the plate and at the same time there was plenty of oxygen for the combustion. In this way the sugar was ignited first, and when the bulb burst the vapor was forced to pass up through the top half of the crucible, which was completely filled with flame. Thus complete combustion was obtained, so that no odor of ester could be noticed in the residual gas, and there was no carbon deposit within the crucible or bomb, but with 35 atmospheres pressure the combustion took the form of an explosion of considerable violence, as the appearance of the crucible testified. In order to reduce the rate of combustion, the concentration of oxygen was therefore diminished; with 20 atmospheres of oxygen everything went smoothly, although the temperature within the crucible was still sufficient to fuse the thin platinum foil, especially where the iron oxide came in contact with it. Afterwards platforms of ignited asbestos paper were substituted for the platinum With the thick asbestos paper there was some tendency toward carbonization in the bottom of the crucible, but with thinner paper this tendency disappeared. The thin asbestos fused together into a globule with the iron oxide—perhaps forming an iron silicate. That this gave rise to no thermal effect was proved by a combustion of sugar alone in which a similar asbestos platform was used. The agreement of this determination with the previous ones also proved the absence of any carbonaceous matter in the asbestos which had escaped combustion in the lower temperature of the Bunsen flame. In this way seemingly complete combustions of the esters, which yielded concordant results, were finally obtained.[1]

Having thus mastered the technique of the combustion of volatile liquids, we returned to the work upon the hydrocarbons, which are far more easily burned than esters. It was not a great surprise to find that the new method yielded results which were higher than those previously found, for the earlier results had been thought too low. In order to make sure, however, that the increase was not due to the presence of combustible matter in the asbestos, very thin glass platforms (made from microscopical cover-glasses) were substituted for the shelf upon which the sugar was to be placed. To review, briefly, the method of combustion for benzene, in its final form, was as follows: the benzene in a very thin glass bulb was placed in the bottom of a narrow platinum crucible, 2 cm. in diameter and 2.5 cm. high. A few millimeters above the bulb was fixed a small platform of thin glass bearing a weighed quantity of powdered sugar. The passage of a current through the coil of iron wire ignited the sugar, which in its turn burst the bulb and ignited the benzene at a moment when the whole top of the narrow crucible was filled with flame from the burning sugar. Thus none of the benzene vapor could escape ignition. The trouble with the old method had been that the larger crucible was too wide. Moreover, the sugar had been beneath the benzene instead of above it, so that some of the benzene escaped unconsumed. The amount which thus escaped was greater when there was more nitrogen present than when there was less. Obviously, with non-volatile compounds like sugar the width of the crucible would make no difference.

---

[1] Although we were not entirely sure of the purity of the esters, they were probably as pure as most organic liquids which have been used by other physico-chemical investigators. Therefore we venture to give, for what they are worth, our results on methyl isobutyrate, which are typical This ester had proved harder to burn than the others mentioned above. Therefore when the method was perfected it was applied to this one first, in order to be sure that it was capable of dealing with the worst cases. In the determination given below no ester smell could be detected and there was no carbon in the bomb The ester supplied by Kahlbaum had been carefully

There follows a series of determinations carried out as described, with always the same quantity of water in the calorimeter.

In a few cases there was conclusive evidence to show that the glass bulb had been broken by pressure previous to the combustion. This

fractionated and dried with calcium chloride, and the fraction boiling between 91.4°–92.0° at 754 mm. was taken. No impurity was detected in this particular sample.

The combustions were made with 8.0 per cent. nitrogen in the bomb.

DATA FOR THE HEAT OF COMBUSTION OF METHYL ISOBUTYRATE.

Therm.	Wt. ester in vacuum.	Observed rise corrected.	Correction for sugar burned.	Correction for iron wire, stirring and HNO_3.	Corrected rise due to ester.	Rise per gram ester
B.........	0.8806	1.739°	—0.126°	—0.020°	1.593°	1.809°
J..........	0.6546	1.358	—0.152	—0.020	1.186	1.812
J..........	0.5147	1.134	—0.135	—0.017	0.932	1.811
J..........	0.6532	1.454	—0.255	—0.018	1.181	1.808
					Average,	1.810

Since a gram of sugar caused a rise of 1.0539° in the same system, methyl isobutyrate on burning is seen to evolve 1.717 times as much heat as an equal weight of sugar. Hence the molal heat of combustion in constant volume of methyl isobutyrate is 2901 kilojoules or 694.0 calories. Thomsen found for the vapor 717.6 calories under constant pressure.

Favre and Silbermann find for methyl butyrate (liquid) 693.4 cal. (*Annales chim. phys.*, [3] 34, 441 (1852).

Heat of vaporization 7.9 cal. (Schiff, *Liebig's Ann.*, 234, 338 (1886)).

was detected by means of the odor of the benzene in the small amount of oxygen always allowed to escape just before the combustion. Such experiments were of course rejected. Otherwise, all the experiments made are recorded in the following table:

HEAT OF COMBUSTION OF BENZENE.

Final Series.

Exp No.	Sample	Per cent N_2	Wt benzene in vacuum	Wt sugar	Change of thermometer corrected	Correction for sugar burned	Correction for iron wire and nitrogen burned and for stirring	Rise due to benzene.	Rise due to 1 gram benzene (weighed in vacuum)
15	B	8 0	0 7763	0 2376	2.347	—0 250	—0 019	2 078	2 677
16	B	8 0	1 0144	0 1050	2 847	— 0 111	0 021	2 715	2 676
17	B	8 0	0 6443	0.2431	1 999	—0 256	—0 019	1 724	2 676
18	B	2 6	0 7480	0.3199	2 355	—0 337	—0.017	2 001	2 675
19	C	2 6	0 7365	0 2522	2 252	-0 266	0 017	1 969	2 674
20	A	2 6	0 7360	0 2068	2 202	—0 218	-0 017	1 967	2 678
21	C	2 6	0 7618	0 2420	2 307	-0 255	- -0 017	2 035	2.672
22	A	2 0	0 6860	0 2823	2 152	-0 298	- 0 018	1 836	2 677
								Average =	2 6750°

Thus one gram of benzene weighed in vacuum evolves enough heat on combustion to raise the special calorimetric system employed 2 675°, the figure having a probable error of 0 0004. The extreme deviation from the mean amounts to less than 0 003°, which, although larger than in the case of sugar, is nevertheless as small as could be expected, considering the complication of the process and the fact that less than a gram of benzene was usually used in the combustion.

Not only is the series satisfactory as a whole, it is also convincing as regards the agreement in several samples of benzene. The average value for Sample B is 2 676°, for A 2 675°, and for C but slightly less, 2 673°. These differences are within the reasonable limit of error, especially since only two determinations of each were made with Samples A and C.

It is interesting to note that the presence of nitrogen has no longer any effect upon the completeness of combustion. Of the eight determinations in the table, the first three were made in the presence of 8 per cent. of nitrogen, whereas in the last five the per cent. of nitrogen was 2 6 or less. The amount of heat evolved in the first three, per gram of benzene, was 2 676, in the last five 2.674. This difference is not greater than the possible experimental error. It is in fact in a direction opposite from that which would have been expected if the difference had any significance. This is a very satisfactory evidence that the combustion was complete in every case, for if it had been incomplete with 2.6 per cent.

of nitrogen, it would have unquestionably been still less complete with 8 per cent.

The only effect of decreasing the nitrogen in our accepted experiments was to cause the correction of nitric acid formed to become noticeably smaller, so that in many instances where the nitrogen amounted to 2.6 per cent. or less, this correction amounted to practically nothing. The actual amounts of nitric acid found were as follows: with 8 per cent. of nitrogen, 0.04, 0.06, 0.03 gram, respectively; with 2.6 per cent. of nitrogen in only two experiments (the second and last) did the amount of nitric acid exceed 0.01 gram.

Circumstantial evidence supported this conclusion that complete combustion of the benzene had at last been obtained. No indications of incompleteness—neither deposited carbon nor residual odor—were perceptible in the bomb after combustion. No test was made for carbon monoxide, because Richards, Henderson and Frevert were unable to find any traces of this gas even with their less efficient method.

In order to show that the first rush of benzene vapor upon the bursting of the bulb in the moment of ignition had not so blown about the powdered sugar that part of it escaped combustion, the following test was made in one case (No. 21). After the combustion the bomb had been rinsed out with very pure water and the nitric acid titrated with sodium hydroxide solution, the sodium nitrate solution was evaporated to dryness in a tared platinum dish. The gain in weight of this dish amounted to 0.0008 gram more than the amount of sodium nitrate calculated from the quantity of sodium hydroxide solution used. Tests by the resorcinol method and with Fehling's solution (after treatment which would have inverted sugar) failed to show any traces of sugar. Even if the gain was really unburned sugar, the temperature rise due to it would have been only 0.0008°, which is beyond the limit of error of the thermometric readings.

Another experiment (No. 22), in which the sugar was compressed into pellets so that it could not be easily blown about, gave a result in perfect agreement with the rest of the series. Benedict and Fletcher[1] have shown that the only important effect of this treatment is a diminution of the speed of reaction.

After one experiment a light deposit of a brownish red powder was found on the walls of the bomb. This proved, upon examination, to be an oxide of iron, obviously without effect upon the value derived from the determination, because the heat of combustion of the iron was always allowed for.

After scores of combustions, the crucibles showed no visible signs of having combined with carbon. The high temperature and the presence of an excess of oxygen undoubtedly prevented this cause of error.

---

[1] This Journal, 29, 753 (1907).

The heat capacity of our calorimetric system has not yet been determined by the method of summing up the water equivalent of the component parts.[1] Thus the results in this paper are to be expressed as ratios, the standard being the temperature rise produced in our calorimetric system by one gram of sugar.

Expressed in this way, our final results are as follows:

Average rise produced in the calorimetric system by one gram of benzene	2.6750°
Average rise produced in the calorimetric system by one gram of sugar	1.0539°
Ratio benzene to sugar = 2.6750/1.0539	2.5382

This is now directly comparable to the results of Richards, Henderson and Frevert. Their ratio of the heats of combustion of like weights of benzene and sugar (when the oxygen was as pure as they could make it) was 2.534. If vacuum corrections for the weights of sugar and of benzene are applied, their value falls to 2.532. Our heat of combustion is thus about 0.26 per cent. higher. This difference was only to be expected, since these investigators clearly showed that their figure was probably less than the true one, on account of the effect of the nitrogen present under the conditions of the earlier experiments. Although the lowering of the heat of combustion was not exactly proportional to the per cent. of nitrogen present, one would have inferred by extrapolation from their experiments that the true value must be about 2.54, in close agreement with our new value 2.538.

Stohmann's ratio for the heat produced by benzene in comparison with that by sugar is 2.5225.[2] This ratio is based upon the determinations for benzene done with the Berthelot bomb. Stohmann also made some earlier determinations with the apparatus of Berthelot and Vieille (a modification of that of Favre and Silbermann), in which the benzene was burned from a lamp in a stream of oxygen. The average of these determinations gave the value 9.977 Calories per gram of liquid benzene at 17°. The ratio derived from this is 2.5275. Thus the results of Stohmann's two series are a little over 0.6 per cent. and 0.4 per cent., respectively, lower than our ratio. Berthelot's[1] ratio is lower still, about 2.520. Julius Thomsen[2] burned benzene vapor, finding a result to which Stohmann applied corrections for the heat of vaporization, using Regnault's formula for the heat of vaporization, and Kopp's value for the molecular heat capacity of liquid benzene. Thomsen's value thus reduced to the heat of combustion in constant volume of liquid benzene at 17° is for a gram of benzene, 10.135 Calories, a value much higher than the others.

---

[1] Richards and Rowe have recently devised a new method for determining specific heats (*Proc. Am. Acad.*, 43, 473 (1908)) and are further perfecting it. It seems probable that with slight modifications their method can be used for the accurate determination of the heat capacity of a bomb. This method is more easily carried out in a chemical laboratory than is the electrical method of Jaeger and von Steinwehr (*Verhandl. d. d. physik. Ges.*, 5, 50 (1903); *Ibid.*, 5, 353 (1903); *Z. physik. Chem.*, 53, 153 (1905))

[2] Stohmann and Langbein, *J. prakt. Chem.*, 45, 313 (1892); 40, 77, 81 (1889); Stohmann, Rodatz and Herzberg, *Ibid.*, 33, 241 (1886).

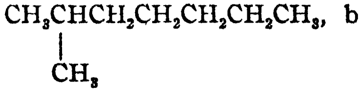
The most probable figure for sugar is that of Fischer and Wrede,[3] who found that a gram of sugar on complete combustion yields 16.545 kilojoules of heat energy. If we accept this value, a gram of benzene is found from our work to yield 2.5382 × 16 545 kilojoules = 41.99 kilojoules. If a kilojoule at 19° is taken as 4.179 Calories, the heat of combustion of a gram of benzene is 10.049 Calories, a result almost as high as Thomsen's.

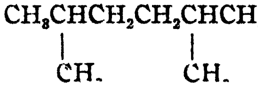
In the more usual and more generally useful standard, 1 mole or gram-molecule of benzene (78.05 grams) evolves 3278 kilojoules. or 784.3 Calories on combustion.

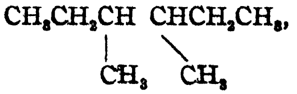
Heats of Combustion of the Octanes.

The next substances whose heats of combustion were studied were five isomeric octanes. These compounds were furnished us by Dr. Latham Clarke, of this laboratory, who is now engaged in an attempt to prepare all the possible isomeric octanes. The octanes burned were:

Normal octane,[4]—$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, boiling point 124.5°.

2-Methyl heptane or iso-octane,[5]  $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_2CH_2CH_3$, boiling point 116.0°.

2,5-Dimethyl hexane or diisobutyl,[6]  $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$, boiling point 108.4°.

3,4-Dimethyl hexane or di-secondary butyl,[7]  $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H\ \underset{\displaystyle CH_3}{\underset{\diagdown}{C}}HCH_2CH_3$, boiling point 116.2°.

---

[1] Berthelot and Vieille, *Ann. chim. phys.*, [6] 10, 458 (1887); Berthelot, *Ibid.*, [5] 23, 193 (1881).

[2] *Thermochemische Untersuchungen*, IV, 59 (Leipzig, 1886).

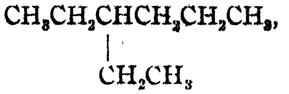
[3] *Z. physik. Chem.*, *Arrhenius Jubelband*, 69, 234 (1909).

[4] Riche, *Ann.* (Liebig), 117, 265; Schorlemmer, *Ibid.*, 162, 280; 147, 227; 152, 152. Zincke, *Ibid.*, 152, 15. Paterno and Peratoner, *Ber.*, 22, 467.

[5] Clarke, THIS JOURNAL, 31, 107 (1909).

[6] Wurtz, *Ann.* (Liebig), 96, 365.

[7] Norris and Green, *Amer. Chem. J.*, 26, 293.

3-Ethyl hexane,[1] 
$CH_3CH_2\underset{CH_2CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$, boiling point 115°.

Great care was taken by Dr. Clarke in the preparation of these compounds and they were undoubtedly purer than most organic liquids of this sort. The earlier preparations formed a small amount of black precipitate on standing over mercury, but the final specimens used in the combustion experiments were practically free from unknown contamination which caused this effect. Careful experimentation showed them to be free from sulphur and halogen, and they were dried by distillation over sodium.

Two samples of 2,5-dimethyl hexane, which had been prepared by different methods, were used. One sample had been prepared by the action of sodium on isobutyl iodide, $(CH_3)_2CHCH_2I$. The other had been prepared by treating acetoacetic ester with sodium and isobutyl iodide. By the action of a magnesium alkyl iodide, the ketone, resulting from saponification of the product obtained above, was reduced to the hydrocarbon. The first sample boiled 0.2° lower than the second and there were also differences of a few units in the fourth decimal place of the densities and in the fifth decimal of the refractive indices, but no differences in the heats of combustion could be detected. In the table, these samples have been marked A (b. p. = 108.3–108.5°) and B (b. p. = 108.1–108.3°). Dr. Clarke considers Sample A slightly purer.

The method of burning the octanes was essentially the same as that used for benzene, except for a slightly different arrangement of the sugar used to start the ignition. In the present case this substance was compressed into pellets, one of which was placed upon the glass plate above the bulb and another, much smaller, was fixed in the coil of iron wire suspended about a millimeter above the large pellet. Another minor modification made in the case of the latter experiments was the invariable use of flattened bulbs instead of spherical ones sometimes employed for holding the liquid. This was especially important because of the considerable compressibility of the octanes; for flattened bulbs are much more flexible than spherical ones, and the danger of their breaking when the bomb is charged with gas is much less.

With the octanes, as with benzene, whenever the bulb broke previous to the combustion, the burning was never complete. Each of these octanes has a characteristic odor and the presence or absence of any smell in the gases after combustion formed a very delicate test of the completeness of the combustion. Whenever the bulb did not break prematurely, the combustion was always complete.

The effect of the amount of nitrogen present in the bomb was tested in the case of one octane (diisobutyl). Since combustions in which the concentration of the nitrogen exceeded 6 per cent. gave results identical with those with only 2 per cent., it was not thought necessary in the other cases to evacuate the bomb before running in the oxygen. The table following gives the rise per gram of octane in the same calorimetric system as that used in the final experiments with benzene. For the last three compounds given in the table the newer form of jacketing apparatus was used. The somewhat increased air space around the calorimeter can involve the heating of more air, but this amount in a system whose heat capacity is nearly 3800 calories is entirely negligible.

---

[1] This substance has not been described in full by Dr. Clarke.

Data Concerning Heat of Combustion of Octanes.

No. of exp.	Name of substance	Designation of sample	Weight octane vacuum. Gram.	Weight sugar vacuum. Gram.	Corr total rise of temperature observed.	Corr. sugar burnt	Corr iron wire stirring HNO_3.	Rise due to octane.	Rise per gram octane.
23	Normal		0.4723	0.1903	1.655°	—0.201°	—0.018°	1.436°	3.040°
24	octane		0.4915	0.1933	1.718	—0.204	—0.019	1.495	3.042
								Average,	3.041
25	Diisobutyl	B	0.6112	0.1521	2.034	—0.160	—0.018	1.856	3.036
26		B	0.6293	0.1045	2.040	—0.110	—0.018	1.912	3.038
27		A	0.5298	0.1395	1.773	—0.147	—0.018	1.608	3.035
28		B	0.5939	0.1381	1.974	—0.145	—0.016	1.813	[3.054[1]]
29		A	0.4944	0.1273	1.656	—0.134	—0.020	1.502	3.038
30		B	0.6606	0.1966	2.234	—0.207	—0.020	2.007	3.038
								Average,	3.037[1]
31	2-Methyl-		0.4340	0.2475	1.599	—0.261	—0.018	1.320	3.041
32	heptane		0.3439	0.2100	1.286	—0.221	—0.017	1.048	3.047
								Average,	3.044
33	3,4-Methyl		0.4283	0.2940	1.628	—0.310	—0.018	1.300	3.035
34	hexane.		0.4681	0.2478	1.702	—0.261	—0.018	1.423	3.040
								Average,	3.038
35	3-Ethyl hexane.		0.3720	0.1428	1.296	-0.150	-0.017	1.129	3.035

---

[1] Experiment 28 is 0.6 per cent. higher than the values for the other experiments, an amount very much greater than can be explained by ordinary experimental error. It is included in the table, because no fault was found in it adequate to account for this discrepancy. The error was probably caused by a mistake in reading one of the thermometers. A single division of the scale (the hundredth of a degree) would have caused the error in question, and every one knows how easy it is to make such a mistake as this. Because of the consistent verdict of the other five experiments, we have not included the result of Experiment 28 in the average. Those who wish to retain it will use 3.040° as the average rise caused by a gram of diisobutyl instead of 3.037°, as given above.

No completed determinations are omitted from the table; all are given which were actually carried out, except those in which the bulb was known to have burst prematurely.

Thus the rises of temperature in our calorimetric system caused by the combustion of the five octanes, namely, the isomeric compounds, normal octane, diisobutyl, 2-methyl heptane, 3,4-dimethyl hexane, and 3-ethyl hexane, were found to be respectively, per gram of liquid, 3.041, 3.037, 3.044, 3.038, and 3.035. The differences are small, but seem to be really significant, because they are distinctly greater than the variations among the individual experiments on any one substance.

In order to express these results in terms of gram-molecules, it is necessary to compare these rises of temperature with those produced by a gram of sugar in order to transform the values into terms of energy. The following table contains these comparisons and gives in the first column the name of the substance, in the second column the rise in our system per gram as given above, in the third column these numbers divided by 1.0539 (the rise of temperature caused by a gram of sugar in the same system), in the fourth column the numbers in the third column multiplied by 16.545, in the fifth column these numbers multiplied by the gram-molecular weight, giving the heat of combustion of 1 mole in kilo joules, and in the last column the same data expressed in terms of calories.

In calculating these results, the molecular weight of the several octanes is taken as 110.11 and the equivalent of one joule is taken as 0.2393 calorie, the value based upon the work of Callendar and Barnes for the 19° calorie, the range over which our experiments were carried out:

HEATS OF COMBUSTION OF FIVE ISOMERIC OCTANES.

(In constant volume, measured at 20°.)

	Rise per gram	Ratio octane to sugar	Heat from 1 gram of hydrocarbon (kilojoules).	Heat of combustion of 1 mole in kilojoules	Heat of combustion of 1 mole in calories
Normal octane . .	3.041°	2.885	47.73	5256	1257
2,5-Dimethyl hexane	3.037	2.882	47.68	5250	1256
2 Methyl heptane. .	3.044	2.888	47.78	5261	1258
3,4-Dimethyl hexane .	3.038	2.883	47.70	5252	1256
3-Ethyl hexane	3.035	2.880	47.65	5247	1255

The five octanes thus have similar heats of combustion, ranging from 5,247 to 5,261 kilojoules, or a range of about one-quarter of 1 per cent. Of the five measured, 3-ethyl hexane has the lowest heat of combustion and 2-methyl heptane the highest. As far as has been discovered by a search into the literature of the subject, no one else has ever determined the heats of combustion of these substances. The differences observed above may represent real differences between the respective energy contents of the five substances; but because only small quantities were available for individual experiments on account of lack of material, the uncertainties of the averages are greater than in the case of benzene. This is especially true with regard to 3-ethyl hexane, of which only one determination was made. Nevertheless it is clear that these isomers are very near together in their heats of combustion, the deviation from the mean value, 5,253 kilojoules, being less than 10 kilojoules on each side, or less than 0.15 per cent. The significance of the figures will be considered later in the summary of all the results.

The Heat of Combustion of the Xylenes.

The only determinations of the heats of combustion of xylenes that have been made before this research was begun were those of Stohmann.[1] He was far from satisfied with the purity of his material, some of which he prepared himself, while part was obtained from the most reliable commercial sources. He neglected in his paper to give boiling points or any other data which might indicate the degree of purity. The combustions themselves were probably more reliable than those of the more volatile hydrocarbons, because of the higher boiling point and less evaporation before combustion, but evidently the figures need thorough revision.

The preparation of pure xylene is by no means an easy matter, as is so often the case with organic compounds. The original material used for the following determinations was the best that Kahlbaum could furnish. The samples had been many times carefully fractionated by electrical distillation in the course of the previous work.[2] Just before being used in the present work the specimens were dried over anhydrous copper sulphate and again distilled. The boiling points, corrected for the projecting thread of the thermometer, were found to be in excellent accord with those found in previous investigations. The following table records these boiling points with the pressures in parentheses, as well as the boiling points given by Schiff[3] and Perkin.[4] Schiff's readings, like ours, were corrected for the protruding column. In Perkin's the thermometer was wholly immersed in the vapor.

BOILING POINTS OF XYLENE.

	Richards and Jesse.	Schiff.	Perkins.
Orthoxylene.......	143.9°–144.2° (763)	141.1° (756.2)	142.6° (760)
Metaxylene........	138.8°–139.2° (761)	139.2° (759.2)	139.3° (760)
Paraxylene........	137.8°–138.1° (754)	138.1° (761.2)	137.5° (760)

About the boiling piont of orthoxylene there seems to be some doubt, the values ranging from 141° to 144°. Neither Schiff's nor Perkin's values agree very well with the present experience, but Woringer[1] has found 143.7°, a value not far from ours.

---

[1] *J. prakt. Chem.*, 35, 40 (1887).

[2] *Z. physik. Chem.*, 61, 449 (1908); THIS JOURNAL, 30, 8 (1908).

[3] *Ann.*, 220, 92; 223, 66.

[4] *J. Chem. Soc.*, 69, 1249 (1896).

These substances were burned in the calorimetric bomb under exactly the same conditions as those used in the case of the octanes. Two of the determinations were vitiated by the premature bursting of the bulb containing the liquid. The experiment was nevertheless continued, to see what would happen, and in these cases a noticeable odor, resembling that of bitter almonds, could be detected afterwards. These, of course, were rejected. In all of the cases excepting the first combustion of paraxylene, the amount of nitrogen present in the oxygen was only two per cent. In this single case it was 6 per cent., but this difference caused no diminution in the heat of combustion. Therefore it is safe to assume that in all the cases the combustion was complete, especially as no odor or sign of deposited carbon was visible in any case. Only in two cases, the first combustion with metaxylene and the first combustion with paraxylene, was enough nitric acid formed to cause 0.001° change in the temperature. In these two cases this correction has been added to the correction for the iron wire burned. The stirring correction was in each case 0.002°, this also has been included with the other. The thermometer numbered B was used in all these determinations:

TABLE—DATA FOR HEAT OF COMBUSTION OF XYLENES.

No. of expt.	Substance.	Wt. xylene vacuum.	Wt. sugar.	Total corr. rise of temperature.	Corr for sugar.	Corr. for wire for stirring and for HNO_3 found.	Rise due to xylene.	Rise per gram xylene.
36	Orthoxylene....	0.6365	0.2421	2.018	—0.255	—0.017	1.746	2.743
37		0.7429	0.3276	2.402	—0.345	—0.016	2.041	2.747
38		0.7307	0.2528	2.288	—0.266	—0.016	2.006	2.745
							Average,	2.745
39	Metaxylene....	0.6871	0.2534	2.171	—0.267	—0.018	1.886	2.745
40		0.7019	0.2008	2.156	—0.212	—0.016	1.928	2.747
41		0.6828	0.3314	2.238	0.349	0.016	1.875	2.743
							Average,	2.745
42	Paraxylene.....	0.5955	0.3190	1 985	—0.336	—0.018	1.631	2.739
43		0.6980	0.2786	2.220	—0.294	—0 016	1.910	2.736
44		0.7380	0.2924	2.342	—0.308	—0.017	2.017	2.733
45		0.5871	0.2260	1.859	—0.238	—0.016	1.605	2.734
							Average,	2.736°

Thus a gram of orthoxylene on burning caused a change of temperature in our calorimetric system of 2.745°; and metaxylene gave precisely the same quantity, within the range of error of our experiments. On the other hand, paraxylene evolved slightly less heat, the temperature in this case rising only 2.736°.

---

[1] *Z. physik. Chem.*, 34, 264 (1900).

There follows a table which translates these temperature changes into terms of energy, similar to the table already given for the five isomeric octanes. In this case, as in the other, the change in temperature produced by a gram of sugar is taken at 1.0539 in our system: the energy represented by the combustion of 1 gram of sugar as 16 545 kilojoules, the large calories as equal to 4 179 kilojoules. The molecular weight of xylene is taken as 106.023.

HEAT OF COMBUSTION OF THREE ISOMERIC XYLENES.

(In constant volume, measured at 20°.)

	Rise of temp per gram.	Ratio of xylene to sugar.	Heat from 1 gram of hydrocarbon, kilojoules.	Heat of combustion of 1 mole in kilojoules.	Heat of combustion of 1 mole in calories
Orthoxylene .. .	2 745°	2 605	43 100	4570 0	1093.5
Metaxylene..... .	2.745°	2.605	43.100	4570.0	1093 5
Paraxylene....	2.736°	2 596	42 951	4554 0	1089.8

The orthoxylene and metaxylene give the same molecular heat of combustion, namely, 4570 kilojoules, or 1093.5 large calories, while the heat of combustion of the para compound is 0.35 per cent. less. Stohmann found for all three values (reduced to the same standard as those employed above) 1084 large calories, or nearly 0 9 per cent. lower than our value for the ortho- and metaxylenes and more than 0.5 per cent. lower than the new value for the paraxylene. This figure is not surprising. Stohmann, as has been said, was much dissatisfied with his determinations, so much indeed that he left the individual experiments unpublished, contenting himself with giving the averages. His hypothetical method of calculating the value from benzene, phenols, etc., need not receive serious consideration, although they yield results not far from ours. A careful survey of the literature seems to leave no doubt that the values given in the above table are by far the most probable of any thus far published.

Theoretical Considerations.

It is interesting now to bring into a single table the several results for the heats of combustion of the various compounds studied in this paper with the idea of comparing them and interpreting their variations. Together with the heats of formation of the several compounds expressed in kilojoules there are given below the boiling points of the various compounds and the approximate latent heats of vaporization. For the xylenes these values have been determined by Richards and Mathews in an investigation soon to be published; but for all but one of the octanes no data are available, and it was necessary accordingly to compute these latent heats according to the rule of Trouton. There are given also in the last column of the table several approximate heats of combustion of the substances in a vaporized condition—simply the sum of the quantities in the two preceding columns:

HEATS OF COMBUSTION OF LIQUID AND OF VAPORIZED HYDROCARBONS.
(In constant volume, determined at 20°)

	Boiling points	Heats of combustion of liquids (kilojoules).	Approximate heats of vaporization.	Approximate heats of combustion of vapors (kilojoules)
Benzene	80.4°	3277	30.8[1]	3308
Orthoxylene........	144.1	4570	37.5[1]	4607
Metaxylene..............	139.0	4570	36.1[1]	4606
Paraxylene...............	138.0	4554	35.6[1]	4590
Normal octane............	124.5	5256	33.8[2]	5290
2,5-Dimethyl hexane.....	108.4	5250	32.0±	5282
2-Methyl heptane........	116.0	5261	33.0±	5294
3,4-Dimethyl hexane ...	116.2	5252	33.0±	5285
3-Ethylhexane............	115.0	5247	33.0±	5280

This table presents several interesting relations, the most important of which may be here briefly summarized:

On comparing the heat of combustion of the liquid benzene, 3277, and the average heat of combustion of the liquid xylenes, 4565, it is evident that the addition of CH_2 causes an increase in the heat of combustion of 644 kilojoules. This is not far from the number found by Thomsen, namely, 671.[3] It probably, more nearly than Thomsen's value, represents the average effect of the addition of CH_2 in a homologous series, because in each of his experiments the liquids with higher boiling points were increasingly in error because of the increasing heat from his "Universal Burner." Accordingly in his work the differences must have been too large. It is evident, nevertheless, that the position of the CH_2 makes an important difference in the result; probably the same value is not to be expected from an aromatic series as from an aliphatic series, and the values are entirely different when oxygen is present.

In spite of these qualifications, the conclusion that the following thermochemical reaction,

$$-\overset{|}{C}H_2 + O_2 = CO_2 + H_2O + 644\text{ kj.},$$

holds true, at any rate in the case of aromatic substances when burnt in constant volume, is the least uncertain of all the theoretical inferences which may be drawn from the present work.

---

[1] Observations by Richards and Mathews, as yet unpublished.

[2] Longuinine, *Compt. rend.*, 121, 557 (1895). The value computed independently by Trouton's rule for the heat of vaporization of normal octane was 34 instead of the value 33.8 found by Longuinine. This close agreement increases one's confidence in the other values calculated in the same way.

[3] This value is found from Thomsen's results from the aromatic hydrocarbons (*Thermochem. Untersuch.*, 4, 221) by subtracting from the average difference (161.8 Calories) corresponding to CH_2 the values 0.6 Calorie for correcting to constant volume, and 0.7 Calorie to allow for the difference of latent heat of evaporation caused by adding CH_2.

Because the heats of combustion of octanes on the average exceed those of the xylenes by 688 kilojoules, one might infer that each gram-atom of hydrogen in combination with carbon caused an increasing heat of combustion of 172 kilojoules. The addition of four hydrogens to each molecule of xylene to make an octane is nevertheless associated with important changes in the relations of the carbon atoms to one another, and these changes may be of considerable thermochemical effect. Hence it is not safe to conclude that a single gram-atom of hydrogen, even when united with carbon, will always increase the heat of combustion by 172 kilojoules, and the futher inference that because CH_2 adds 644 and H_2 adds 344 a single carbon would cause 300 kilojoules additional heat is likewise uncertain.[1]

Enough evidence has been collected to suggest the possibility of finding yet other interesting and fundamental relations and to make the collection of many more figures of the highest accuracy desirable. It will be necessary to investigate with the utmost precision a great number of typical cases of all kinds, in order to be sure of any generalization. In the fulfilment of this program, it is hoped that further careful work of this kind may be undertaken at Harvard University in the immediate future.

In conclusion it is a pleasure to express our indebtedness to the Carnegie Institution of Washington for generous pecuniary assistance in the prosecution of this work.

Summary.

In further prosecution of the revision of thermochemical data, the heats of combustion of benzene and a number of octanes and xylenes were determined with unusual care. The object in choosing these substances was to endeavor to trace the effect of constitution or arrangement upon the heats of formation of isomeric substances and thus to obtain a more definite idea of the relation of total energy change to structure. Octanes in particular were chosen because the molecule is large enough to admit of considerable variety in the isomeric compounds, but not so large as to confuse the relationships. Simplicity in interpretation is also gained by having only two elements present. The hydrocarbons were prepared in a state of great purity by Dr. Latham Clarke, according to methods worked out several years ago for this purpose. In the execution of this work the adiabatic method of calorimetry was used with great success and in general the precautions used in previous work of this kind were adopted throughout, with several new improvements. The volatile liquids were sealed in flexible flattened glass bulbs and ignited by means of small weighed quantities of sugar placed above the bulb on a glass shelf, the substances both being contained in a very small narrow platinum crucible. When conducted in this way, the combustion was in every case complete; with a wider crucible the combus-

---

[1] See W. A. Noyes, "Organic Chemistry," pp. 44, 80, 85, 90, and 162.

tion was not always complete. The final results showed very satisfactory agreement among themselves.

In this way it was found that the heats of combustion of the following substances possess relative magnitudes, indicated by the numbers following the respective names: sugar, 1 0000; benzene, 2 5382; orthoxylene, 2 605; metaxylene, 2 605; paraxylene, 2 596; normal octane, 2 885; diisobutyl, 2 882; 2 methyl heptane, 2 888; 3,4 dimethyl hexane, 2.883; 3-ethyl hexane, 2 880 If the heat of combustion of sugar is taken with Fischer and Wrede as 16 545 kilojoules per gram and O = 16 000 is taken as the standard of molecular weight, the molal heats of combustion of the nine liquid hydrocarbons (in kilojoules, determined in constant volume at 20°) are as follows, respectively: benzene, 3,278; orthoxylene, 4570; metaxylene, 4570; paraxylene, 4554; normal octane, 5256; diisobutyl, 5250; 2-methyl heptane, 5261; 3,4-dimethyl hexane, 5252; 2-ethyl hexane, 5247 kilojoules. The deviations from one another, shown by the simple isomers, are comparatively small. The addition of CH_2 in aromatic compounds is seen to cause an increase in this heat of combustion of 644 kilojoules, or 154 Calories.

The differences between the isomers are so small that an attempt at definite explanation of their causes would be premature. Much more work of the most precise nature is necessary to afford firm basis for theory. It is hoped that this investigation will be continued, and that in the near future further data of this kind will be obtained in the laboratory of Harvard College, where these researches were made.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.

FIRST PAPER.—THE ANALYSIS OF SILVER PHOSPHATE.

BY GREGORY PAUL BAXTER AND GRINNELL JONES.

Received January 14, 1910.

Although phosphorus is one of the best known and most important elements, present knowledge concerning its atomic weight is somewhat inadequate. The early determinations of this constant by Dulong,[1] Pelouze,[2] Berzelius,[3] and Jacquelain[4] are widely discrepant and have no particular significance. Those by Schrötter, Dumas, van der Platts, and Berthelot, on the other hand, all give values not far from 31.0, and this value has been selected by the International Committee on Atomic Weights. Although these investigations have already been critically

[1] *Ann. chim. phys.*, 2, 149 (1816).

[2] *Compt. rend.*, 20, 1053 (1845).

[3] Lehrbuch, 5th Ed., 3, 1188 (1845).

[4] *Compt. rend.*, 33, 693 (1851).

discussed by Clarke,[1] Brauner,[2] and others, a few of the more important sources of error are briefly pointed out here.

Schrötter,[3] the discoverer of red phosphorus, converted weighed quantities of this substance into phosphorus pentoxide by combustion in a stream of oxygen. As the mean of ten determinations which varied from 30.94–31.06, he obtained 31.03 for the atomic weight of phosphorus. The oxygen used was slightly moist, as Brauner has pointed out, since, although it was dried by phosphorus pentoxide, it was finally passed through a tube containing calcium chloride! The phosphorus pentoxide formed during the combustion must have retained this small amount of water, which would make the atomic weight of phosphorus appear too low. Schrotter admits that the combustion was incomplete, and since this error would tend to raise the atomic weight of phosphorus, he concludes that the true value is 31.00

Dumas[4] titrated the trichloride of phosphorus against silver after decomposing the trichloride with water. Since the sample used did not boil at a constant temperature but distilled between 76° and 78°, it must have been impure. If it contained oxychloride, as Clarke has suggested, the atomic weight of phosphorus would be found too high. Dumas overlooked the solubility of silver chloride and therefore used the wrong end-point in these titrations. Furthermore, no precautions are mentioned either for preventing access of water to the material before weighing or for preventing the reduction of the silver salt by the phosphorous acid formed in the decomposition of the trichloride with water. Recalculated on the basis of the atomic weight of silver as 107.88, his five analyses give results which vary between 30.99 and 31.08. The average is 31.03.

Van der Platts[5] made two determinations by each of three different methods. He obtained the values 30.90 and 30.97 by the precipitation of silver from silver sulphate solution with phosphorus. His results from the analysis of silver phosphate were 31.08 and 30.95. He gives no details of the method of preparing and analyzing this substance, merely making the statement: "It is difficult to be sure of the purity of this salt." Finally, by the combustion of yellow phosphorus in oxygen he obtained the results 30.99 and 30.96. The very meager descriptions of these experiments preclude criticism.

Using Leduc's data for the densities and compressibilities of phosphine and oxygen, Daniel Berthelot[6] has calculated, by the method of limiting densities, the molecular weight of phosphine to be 34.00 and the atomic weight of phosphorus to be 30.98.

---

[1] "A Recalculation of the Atomic Weights," Smith. Misc. Coll., 1897.

[2] Abegg, "Handb. der anorg. Chem.," 1907, Vol. III, Part 3, p. 366.

[3] *Ann. chim. phys.*, [3] 38, 131 (1853).

[4] *Ann. Chem. Pharm.*, 113, 28 (1860).

[5] *Compt. rend.*, 100, 52 (1885).

[6] *Ibid.*, 126, 1415 (1898).

Very recently Gazarian[1] has obtained a considerably lower value for the molecular weight of phosphine, 33.93. This value was calculated from the experimentally determined weight of the standard liter by the four methods of molecular volumes (Leduc), limiting densities (Berthelot), critical constants (Guye), and "indirect" limiting densities (Berthelot). The different methods give essentially identical results, except in the case of the direct method of limiting densities. By the latter method a value six-hundredths of a unit higher is obtained, but Gazarian rejects the result on the basis of inaccurate knowledge of the compressibility of phosphine. It is highly desirable to obtain more certain knowledge of the compressibility of phosphine, since the method of limiting densities is the most reliable of all the methods for applying the correction to the densities made necessary by deviations from the laws of a perfect gas.

The other methods are burdened with arbitrary assumptions and empirical constants, and furthermore Baumé[2] has shown that both the method of molecular volumes and the method of critical constants give correct results only with gases for which the ratio $\frac{T_c}{4P_c}$ is nearly 1, whereas for phosphine this ratio is 1.26.

If the molecular weight of phosphine be assumed to be 33.93, the atomic weight of phosphorus is 30.91. In the light of this low result it is unfortunate that Gazarian prepared phosphine by only one method, and that he did not determine the purity of the gas, *i. e.*, by absorption. Gazarian used the method of Matignon and Trannoy[3] which consists in heating calcium phosphate and aluminium together until they react, and then treating the product of this reaction without further purification with water in a gas generator. Matignon and Trannoy show that the gas prepared in this way by them contained about 3 per cent. of hydrogen, probably derived from calcium contained by the phosphide. In this case some calcium nitride would be formed, since the phosphide was made in air, and this would produce ammonia as an impurity in the phosphine. Although the gas was purified by fractional distillation, according to Gazarian's statements hydrogen is difficult to eliminate, and a proportion of only four-tenths of 1 per cent. would be sufficient to lower the atomic weight of phosphorus one-tenth of a unit. Ammonia would be even more difficult to remove, since its boiling point is only 50° higher than that of phosphine. The effect of a given percentage of impurity is, however, much less with ammonia than with hydrogen, although in the same direction.

---

[1] *J. chim. phys.*, 7, 337 (1909).

[2] Baumé, *J. chim. phys.*, 6, 76 and 86 (1908).

[3] *Compt. rend.*, 148, 167 (1909).

From the preceding brief summary it is evident that the uncertainty in the atomic weight of phosphorus is as great as one-tenth of a unit, and that, as Brauner remarks at the conclusion of his review of the subject, "a revision of the atomic weight of phosphorus with modern means is urgently necessary."

The analysis of silver phosphate was selected as one of the most promising methods of attacking the problem, since the per cent. of silver can be determined exactly by a method which has been carefully studied, especially in this laboratory. The accuracy of the result will therefore depend primarily upon the success attained in preparing silver phosphate in a perfectly definite and pure state. The greater part of the following research was devoted to the solution of this problem, which van der Platts found so difficult.

The analysis of the halogen compounds of phosphorus offers certain difficulties, owing to the ease with which these substances are decomposed by water, and to the necessity for oxidizing the phosphorous acid resulting from the decomposition of the halogen compounds with water before the addition of silver nitrate. An investigation upon the tribromide of phosphorus is now in progress in this laboratory. Phosphonium compounds were found utterly unsuited for exact analysis on account of their instability.

Purification of Materials.

Water.—All the water used in this research was made from the laboratory supply of distilled water by distillation, first from an alkaline permanganate solution, and then, after the addition of a trace of sulphuric acid, through a block-tin condenser.

Ammonia.—The best commercial ammonia was distilled into the purest water.

Nitric Acid.—The best commercial concentrated acid was twice fractionally distilled through a platinum condenser, with the rejection of the first third of the distillate. Every sample was shown to be free from chloride by careful nephelometric tests.

Hydrochloric Acid.—The best commerical C. P. acid, diluted with an equal volume of water, was distilled through a platinum condenser.

Hydrobromic Acid.—This substance was prepared in conjunction with Mr. F. B. Coffin, who was engaged in a parallel research upon the atomic weight of arsenic.[1] Commercial bromine was converted into potassium bromide by addition to recrystallized potassium oxalate. In a concentrated solution of this bromide, in a distilling flask cooled with ice, bromine was dissolved, and distilled from the solution into a flask cooled with ice. A portion of the purified bromine was then converted into potassium bromide with pure potassium oxalate as before, and the remainder of the bromine was distilled from solution in this pure potassium bromide. The product obtained was thus twice distilled from a bromide, the bromide in the second distillation being essentially free from chlorine. This treatment has already been proved sufficient to free bromine from chlorine.[1]

---

[1] Baxter and Coffin, THIS JOURNAL, 31, 297 (1909).

Hydrobromic acid was synthesized from the pure bromine by bubbling hydrogen gas (made by the action of water on "hydrone") through the bromine warmed to 40-44° and passing the mixed gases over hot platinized asbestos in a glass tube. The apparatus was constructed wholly of glass. The hydrogen was cleansed by being passed through two wash-bottles containing dilute sulphuric acid, and through a tower filled with beads also moistened with dilute sulphuric acid. The hydrobromic acid gas was absorbed in pure water contained in a cooled flask. In order to remove iodine the solution of hydrobromic acid was diluted with water and twice boiled with a small quantity of free bromine. Then, a small quantity of recrystallized potassium permanganate was added to the hydrobromic acid solution, and the bromine set free was expelled by boiling. Finally the acid was distilled with the use of a quartz condenser, the first third being rejected. It was preserved in a bottle of Nonsol glass provided with a ground-glass stopper.

The purity of the hydrobromic acid was tested by a quantitative synthesis of silver bromide. The silver used, which was kindly furnished by Mr. G. S. Tilley, had been prepared with all the necessary precautions for work on the atomic weights of silver and iodine.[2] The procedure used by Baxter[1] for the synthesis of silver bromide from a weighed amount of silver was followed in detail. In this experiment 6.02386 grams of silver yielded 10.48627 grams of silver bromide; hence, silver bromide contains 57.4452 per cent. of silver, while Baxter found as the mean of 18 determinations 57.4453 per cent. The hydrobromic acid was evidently pure.

Silver Nitrate.—Crude silver nitrate was reduced with ammonium formate, made by passing ammonia gas into redistilled formic acid. The reduced silver was washed with the purest water, until the wash-waters no longer gave a test for ammonia with Nessler's reagent, and was fused on sugar charcoal. The buttons were then scrubbed with sea-sand and thoroughly cleansed with ammonia and nitric acid. They were then dissolved in redistilled nitric acid, in a platinum dish. After the silver nitrate solution had been evaporated on a steam bath until saturated, an equal volume of redistilled nitric acid was added and the solution was cooled. The precipitated silver nitrate was very completely drained in a centrifugal machine, provided with platinum Gooch crucibles to retain the salt.[1] A similar recrystallization followed. The final product was preserved in Jena glass vessels under a bell-jar.

---

[1] Baxter, This Journal, 28, 1322 (1906).

[2] Baxter and Tilley, *Ibid.*, 31, 201 (1909).

Disodium Phosphate.—One kilogram of Merck's best disodium phosphate was dissolved in hot water in a porcelain dish and hydrogen sulphide passed into the solution for several hours. After standing for twenty-four hours, the solution was again heated, saturated with hydrogen sulphide and filtered. The filtrate was slightly green, owing to the presence of iron. The solution was boiled to expel the hydrogen sulphide and a small amount of green precipitate filtered out. The filtrate was still distinctly green. The sodium phosphate was then crystallized fifteen times, five times in porcelain with centrifugal drainage of the crystals in a large porcelain centrifugal machine, ten times in platinum vessels with centrifugal drainage of the crystals in platinum Gooch crucibles. The green color concentrated in the first mother liquor.

When tested by means of the Marsh test, this material was found to contain only a mere trace of arsenic, which was estimated to be 0.01 mg. in 10 grams of the salt. This small amount could have no effect on the analytical results, especially since the percentage of silver in silver arsenate is nearly the same as in silver phosphate. By means of the nephelometer it was proved that this material contained no chloride or other substances which could be precipitated by silver nitrate in the presence of dilute nitric acid.

Sodium Ammonium Hydrogen Phosphate.—The best commercial microcosmic salt was recrystallized four times in platinum vessels. It was tested for arsenic by Marsh's method with negative results and gave no opalescence visible in the nephelometer when tested with silver nitrate and dilute nitric acid.

Preparation of Trisilver Phosphate.

Silver phosphate was prepared by mixing dilute solutions of silver nitrate with solutions of sodium and ammonium phosphates. Since it is not feasible to purify silver phosphate by recrystallization, the conditions of precipitation must be so chosen that a pure product will be obtained at once.

In order to avoid inclusion and occlusion of silver nitrate, sodium nitrate, sodium phosphate, or mono- or disilver phosphate, all of the solutions for precipitation were made about 0.03 *N*. All samples after precipitation were thoroughly washed and allowed to stand in water for at least twenty-four hours, in order to convert occluded acid phosphates into trisilver phosphate. Qualitative tests for nitrate with diphenylamine and for sodium by the spectroscope showed that all of the first three substances named could be completely washed out.

---

[1] Baxter, This Journal, 30, 286 (1908).

Joly[1] states that disilver phosphate is stable in the presence of phosphoric acid containing 40 per cent. (11.8 *N*) of phosphoric anhydride, but is transformed into trisilver phosphate if the acid contains 38 per cent. (11.0 *N*) or less phosphoric anhydride. Since all the solutions used for the preparation of silver phosphate were nearly neutral, it is evident that the precipitation of disilver phosphate as a distinct phase in equilibrium with the solution is not to be feared.

It is, however, not such a simple matter to prove the absence of *occluded* disilver hydrogen phosphate or monosilver hydrogen phosphate. Much light is thrown on this point in a recent paper by Abbott and Bray[2] upon the dissociation constants of the three hydrogens of phosphoric acid, which were found to be 1.1×10^{-2}, 1.95×10^{-7} and 3.6×10^{-13} respectively. Since phosphate ion ($PO_4^{\equiv}$) is almost completely hydrolyzed to monohydrophosphate ion ($HPO_4^{=}$), even in slightly alkaline solutions, and since in slightly acid solutions dihydrophosphate ion ($H_2PO_4^-$) acquires an appreciable concentration, the possibility of occlusion must be examined with special care.

The concentrations in the following table are either taken directly from a table given by Abbott and Bray or calculated from these numbers with the help of the values of the dissociation constants of phosphoric acid. The values are expressed in formular weights per liter, the total concentration of the salt being in each case 0.05.

	$NaNH_4HPO_4$.	$Na_2NH_4PO_4$.
$H_2PO_4^-$	0.001184[3]	0.000002[4]
$HPO_4^{=}$	0.03265[3]	0 03219[3]
$PO_4^{\equiv}$	0.0000016[4]	0.001123[3]
OH^-	0.00000079[3]	0.000502[3]
H^+	0.0000000075[4]	0 000000000012[4]

It will be noted that the replacement of the remaining hydrogen in sodium ammonium hydrogen phosphate by sodium decreases the concentration of the hydrogen ion to 0.16 per cent. of its value in the microcosmic salt solution and decreases the concentration of dihydrophosphate ion to 0.2 per cent. of its former value. The concentration of monohydrophosphate ion remains essentially unchanged, while the concentration of phosphate ion is increased seven hundred times. Disodium phosphate doubtless takes a position intermediate between the other two solutions

---

[1] *Compt. rend.*, 103, 1071 (1886).

[2] This Journal, 31, 755 (1909).

[3] These values are taken directly from the table of Abbott and Bray.

[4] These values are calculated from the others in the above table by the aid of the following equations:

$$(H^+)(OH^-) = 0.59 \times 10^{-14}$$

$$\frac{(H^+)(PO_4^{\equiv})}{(HPO_4^{=})} = 3.6 \times 10^{-13} \qquad \frac{(H^+)(HPO_4^{=})}{(H_2PO_4^-)} = 1.95 \times 10^{-7}$$

in this regard, since it is more alkaline than microcosmic salt and less so than disodium ammonium phosphate. The numbers given above refer to solutions which are five times as strong as those used in this research, but the conditions in the more dilute solutions must be very similar. Furthermore, the exact values have no great importance, as the concentrations of the various ions change continuously during precipitation. It is evident from the figures given above and from the value of the dissociation constant of the second hydrogen of phosphoric acid that if the concentration of hydrogen ion increases above its value in a microcosmic salt solution, the concentration of dihydrophosphate ion must increase greatly at the expense of monohydrophosphate ion. If there is any tendency for the occlusion of disilver hydrogen phosphate or monosilver hydrogen phosphate, the amounts of these salts occluded would be expected to depend on the concentration of the undissociated molecules of these salts in the solution, and therefore on the concentration of silver ion and on the concentration of monohydrophosphate or dihydrophosphate ion respectively.

The exact concentrations of the ions during the precipitation cannot be calculated, since the solubility of silver phosphate in slightly acid solutions and the solubility-product of silver phosphate are not known. It is, however, easy to understand from a study of the conditions under which the various samples of silver phosphate were precipitated, that these concentrations must have varied greatly in the preparation of the different samples and therefore constancy of composition gives a strong presumption that there is very little or no tendency for the occlusion of the undesired acid salts.

Samples N and O.—A 0.03 normal solution of silver nitrate was slowly poured into a 0.03 normal solution of disodium hydrogen phosphate with frequent shaking. This reaction may be roughly considered to take place in two stages represented by the equations:

$$3AgNO_3 + 2Na_2HPO_4 = Ag_3PO_4 + NaH_2PO_4 + 3NaNO_3$$
$$3AgNO_3 + NaH_2PO_4 = Ag_3PO_4 + NaNO_3 + HNO_3$$

At the beginning of the precipitation the solution is very slightly alkaline and remains very nearly neutral during the addition of the first half of the silver nitrate. The concentration of the silver ion is kept very low by the excess of phosphate and, therefore, little occlusion of the acid salts is to be expected in spite of the fact that the solution contains appreciable concentrations of the monohydrophosphate and dihydrophosphate ions. The precipitate during this stage is very finely divided and does not settle well and, therefore, no attempt was made to collect it separately.

During the addition of the second half of the silver nitrate the solution becomes slightly acid and the solubility of the silver phosphate increases rapidly. The precipitate settles readily. During the second stage the conditions are more favorable for the occlusion of the acid phosphate, but only a small amount of silver phosphate is precipitated during this stage.

After standing a short time the mother liquor was decanted from the precipitate, and exactly the calculated amount of redistilled ammonia, diluted to one liter, was added to neutralize the excess of acid and complete the precipitation. Since this sample was evidently produced from a solution which was slightly acid at the beginning of the precipitation, although very nearly neutral at the end, and since it contained a considerable amount of silver, the conditions were favorable for the formation of acid salts.

Both precipitates were transferred to a large platinum dish and washed many times by decantation with the purest water. This washing was prolonged over more than twenty-four hours in order to give time for all soluble matter to be leached out. When the precipitates were tested for nitrate with diphenylamine, negative results were obtained. Sodium was found to be absent by spectroscopic tests The precipitates were drained as far as possible in a platinum centrifugal machine, and the drying was completed by heating in platinum crucibles in an electric air bath for several hours, first at 90° and finally at about 130°. The dried lumps of silver phosphate were then gently ground in an agate mortar. The samples were preserved in platinum crucibles over sulphuric acid in the dark. All of the operations were performed in a dark room.

The sample prepared by pouring silver nitrate into disodium phosphate is designated Sample N, and the sample prepared by adding ammonia to the mother liquors is designated Sample O.

Sample P—A 0.03 normal solution of disodium ammonium phosphate was prepared by dissolving a weighed amount of disodium hydrogen phosphate and then adding the calculated amount of redistilled ammonia. The solution was then slowly poured into a 0.03 normal solution of silver nitrate. By this method of precipitation the solution is maintained as nearly neutral as is possible, because the excess of silver prevents the concentration of phosphate in solution from exceeding a very small value, so that neither can the solution become alkaline by hydrolysis nor can the concentration of hydrophosphate attain an appreciable value. The absence of the hydrophosphate ions would be expected to prevent the formation and occlusion of acid silver phosphate in this sample, whereas in Sample N the same result is probably brought about by the absence of the silver ion. Unfortunately both of these favorable conditions cannot be combined in one precipitation, as will be shown later. This precipitate settled readily. The washing, testing, and drying were carried out as already described for Samples N and O. This sample is designated Sample P.

Sample R.—A 0.03 normal solution of sodium ammonium hydrogen phosphate was slowly poured into a similar solution of an equivalent amount of silver nitrate. Under these conditions the solution contains an excess of silver, which tends to produce occlusion of acid phosphates, since the solution becomes more and more acid as the precipitation proceeds, and as the precipitation is therefore far from complete, the concentrations of the two hydrophosphate ions gradually approach a very considerable value. At no stage could the solution become alkaline by hydrolysis. It should be noticed that the procedure differs from that used in preparing Sample N in that the precipitate is formed in the presence of an excess of silver nitrate instead of an excess of phosphate, and that this difference in the method of mixing greatly changes the conditions of precipitation.

The precipitate, which was designated Sample R, coagulated and settled quite readily. The washing and drying were completed as usual.

It will be shown that samples of silver phosphate prepared under these various conditions have nearly, if not exactly, the same composition. Further proof of the absence of acid phosphate in these samples is given by experiments to be described later which show that no water is given off when this material is fused.

An attempt to prepare a sample by pouring silver nitrate into disodium ammonium phosphate yielded unsatisfactory results. Since the disodium ammonium phosphate solution was alkaline, owing to hydrolysis, it contained free ammonia, which prevented the precipitation of silver phosphate at first. Nearly one-quarter of the silver nitrate was added before a permanent precipitate was produced. At the end of the precipitation the solution was of course essentially neutral. Even after standing for four days the precipitate had not appreciably settled. Since the coagulation of the precipitate seems to occur much more readily in the presence of excess of silver, a considerable amount of silver nitrate in solution was added. The precipitate coagulated and settled immediately. It was washed and dried as usual. This sample was somewhat darker in color than the other samples and gave a large amount of insoluble residue when treated with dilute nitric acid. The analysis showed that it contained about two hundredths per cent. too much silver. This method of preparation is evidently unsatisfactory.

Three unsuccessful attempts were made to prepare silver phosphate from trisodium phosphate. The samples obtained in this way did not appear homogeneous after being dried and contained considerable sodium in spite of protracted washing. Two of these samples were found by analysis to contain, respectively, 4.4 and 4.1 per cent. less silver than pure trisilver phosphate. The third of these samples was so unsatisfactory in appearance and in its behavior during its preparation that it was not analyzed. This method of preparing silver phosphate is evidently not suitable for our purpose. Time was lacking to investigate further this anomalous behavior.

Method of Analysis.

Unfortunately, owing to the high melting point of silver phosphate, it was not feasible to fuse the silver phosphate before its analysis in order completely to eliminate all water. Instead it was heated in a platinum boat, in a current of pure dry air, at a temperature of about 400° for seven hours, and then by means of bottling apparatus[1] it was enclosed in its weighing-bottle without coming in contact with the moist air of the laboratory. During this heating the access of light to the sample was prevented. The continuous current of air which passed over the silver phosphate during the heating was driven by a water pump successively through an Emmerling tower containing beads moistened with silver nitrate solution, through a tower containing small pieces of fused caustic potash, then through three towers containing beads drenched with concentrated sulphuric acid, and finally through a long tube containing phosphorus pentoxide which had been resublimed in a current of air. The hard glass tube containing the platinum boat was surrounded by blocks of aluminium[2] which were jacketed with asbestos on the top and sides and heated directly from below by a large burner. The platinum boat was not attacked in the least, as was shown by the fact that its weight remained constant.

It was feared that in spite of this prolonged heating the silver phosphate still retained a trace of water, but by making the conditions in the different experiments as nearly uniform as possible it was hoped that the amount of water retained would be constant. Proof will be given later that the drying was highly efficient.

The salt thus prepared for analysis was allowed to stand over night in a desiccator covered with a black cloth in the balance room, and was then weighed in its glass-stoppered bottle by substitution, with the use of another weighing-bottle of very similar surface and volume as a counterpoise.

The balance was a nearly new No. 10 Troemner balance. It was easily sensitive to 0.02 mg. The weights had already been used in an investigation of the atomic weight of sulphur,[3] and were restandardized with a very gratifying result. None of the corrections found differed by as much as 0.02 mg. from those found a year before, and only a few by

---

[1] Richards and Parker, *Proc. Amer. Acad.*, 32, 59 (1896).

[2] Baxter and Coffin, *Loc. cit.*

[3] Richards and Jones, THIS JOURNAL, 29, 826 (1907).

0.01 mg. The balance was provided with a few milligrams of radium bromide of radioactivity 10,000 to dispel electrical charges generated during the handling of the weighing-bottles with cork-tipped pincers.

The platinum boat containing the silver phosphate was transferred to an Erlenmeyer flask of "non-sol." glass of one liter capacity and treated with about 30 cc. of 5 normal nitric acid. Solution took place rapidly. The solution was not perfectly clear, however, owing to a very slight insoluble residue which sometimes settled out on standing. The solution was then heated on a steam bath until the residue dissolved completely. Upon the addition of about one liter of cold water a very slight opalescence was produced, which was visible only when the solution was carefully examined in a very favorable light. The solution was again warmed until it became perfectly clear. The water and nitric acid used in these processes did not give an opalescence visible in the nephelometer when treated with silver nitrate. The nature of this residue will be discussed more in detail after describing the remainder of the analytical process.

About 800 cc. of water were placed in a large glass-stoppered precipitating flask and a very slight excess of hydrobromic acid was added from a burette. The silver phosphate solution was then very carefully poured into the hydrobromic acid solution. This method of precipitation gives less opportunity for the occlusion of silver phosphate or nitrate than the reverse method. The occlusion of hydrobromic acid can do no harm. The flask was shaken for twenty minutes and was allowed to stand for several days until the precipitate had completely settled. Then the precipitate was collected upon a weighed Gooch crucible after many rinsings with pure water. In order to protect the mat of the Gooch crucible from disintegration, it was covered by a circular disk of thin platinum foil, perforated with many small holes. The precipitate was dried in an electrically heated air bath for several hours at 90°, then for some time at 130°, and finally for at least eight hours at 180°. After the crucible containing the precipitate had been weighed, the silver bromide was transferred to a porcelain crucible and the loss on fusion determined. The presence of the platinum disk covering the mat makes it possible to transfer very nearly all the silver bromide to the porcelain crucible without contamination with asbestos and therefore it is unnecessary to correct the loss on fusion for the small amount of silver bromide which is not fused. The loss on fusion, which represents water remaining in the silver bromide, was subtracted from the weight of the silver bromide. The asbestos shreds carried away by the wash-waters and any silver bromide which may have escaped the Gooch crucible were collected by passing the filtrate through a very small filter paper. The paper was then burned and the residue, after treatment with a drop of nitric and hydrobromic acids to convert any reduced silver into silver bromide, was again gently heated and finally weighed. The weight of the asbestos, corrected for the ash of the paper, was added to the weight of the silver bromide. In order to determine the soluble silver bromide, the filtrate was evaporated until most of the excess of nitric acid was driven off. The precipitating flask and all the flasks which had held the filtrate were rinsed with strong ammonia and the rinsings added to the evaporated wash-water. Enough ammonia was added to make the solution alkaline and it was then diluted to 100 cc. in a graduated flask. The amount of silver bromide present was determined by comparison in the nephelometer with a very similar solution containing a known amount of silver bromide. Both precipitates were dissolved in ammonia and reprecipitated at the same time and under precisely similar conditions[1] in the nephelometer tubes by a slight excess of nitric acid. The amount found in this way was added to the weight of the silver bromide.

In order to determine whether silver phosphate is occluded by silver chloride, about 6 grams of silver phosphate were dissolved in nitric acid and the solution was diluted and poured into an excess of hydrochloric acid. After standing until the supernatant liquid was clear, the precipitate was washed very thoroughly with water and then dissolved in redistilled ammonia. The solution was diluted to one liter and the silver chloride was reprecipitated with nitric acid. The precipitate was filtered out and the filtrate evaporated in a platinum dish until concentrated. A little sodium carbonate was added and the dish was heated to expel all volatile ammonium salts. The residue was dissolved in about 3 cc. of water and treated with an excess of ammonium molybdate reagent with gentle warming. After standing for three days, not the slightest precipitate or yellow color had appeared, showing that no phosphate had been occluded by the silver chloride. Although not tested experimentally, it is reasonable to suppose that silver bromide also does not possess the property of occluding appreciable quantities of silver phosphate or phosphoric acid.

Insoluble Residue.

The presence of a slight residue or opalescence, after dissolving the dried silver phosphate in dilute nitric acid, proved the most perplexing difficulty which was encountered. The effort to discover the nature of this insoluble matter and eliminate it consumed a large part of the time devoted to this research. In an effort to make sure that it was not due to some unknown impurity, nineteen different samples of silver phosphate were prepared, the source of material, method of purification, and precipitation being varied. Disodium phosphate, trisodium phosphate, and sodium ammonium phosphate were carefully purified and converted into silver phosphate under varying conditions without appreciable effect upon the amount of the residue. Phosphorus oxychloride was twice fractionally distilled, converted into phosphoric acid, and then into disodium phosphate by means of sodium hydroxide made from sodium amalgam. The product was crystallized three times. Silver phosphate made from this material gave a slight residue, very similar to that obtained from the best samples made in other ways. Unfortunately, it was necessary to reject the analytical results obtained with this specimen because it was found to contain a small amount of metaphosphate. We did not succeed in preparing a sample of silver phosphate entirely free from the residue.

---

[1] See Richards and Staehler, This Journal, 29, 635 (1907).

In the meantime attention had been devoted to the residue itself. The small amount of material available rendered this part of the investigation difficult. The silver phosphate, after its precipitation and washing, but undried, dissolves in dilute nitric acid, giving a solution which is perfectly clear to the naked eye, although some samples gave a barely visible opalescence in the nephelometer. The opalescence was much too small to have any effect on the analytical results. The dried samples invariably gave an opalescence.

Dry silver phosphate is very slowly darkened in color by the action of light. This effect is even more pronounced when silver phosphate is exposed to the light in the presence of water. These darkened samples gave a much greater residue than the undarkened material. The residue was insoluble in ammonia, slowly soluble in dilute nitric acid, especially when heated, and readily soluble in strong nitric acid. The addition of hydrochloric acid to these nitric acid solutions gave a precipitate of silver chloride, while ammonium molybdate indicated the presence of phosphate.

In order to determine whether or not a loss of weight occurs during the darkening by light, a sample of silver phosphate was dried and weighed as usual and found to weigh 3.01901 grams. It was then exposed to the direct action of bright sunlight for a day, while contained in a weighing bottle which was placed in a desiccator over sulphuric acid. It was found to have darkened slightly in color and to weigh 3.01903. The gain of 0.02 mg. is within the limit of error in the weighing. This sample, when treated with dilute nitric acid, gave a much larger residue than usual, which weighed 1.8 mg. This is much more residue than was usually found in samples containing 4–8 grams of silver phosphate. It is estimated that the samples which had been protected from the action of light as much as possible, except when unavoidably exposed to diffused daylight while being weighed or transferred to the furnace and solution flask, contained about one one-hundredth of a per cent. of this residue.

Two analyses were made of the residue obtained by exposing silver phosphate *under water* to the action of light for several days, then dissolving the excess of silver phosphate in dilute nitric acid and thoroughly washing and drying the residue. 0.02674 gram of this residue yielded 0.03551 gram of silver chloride, which indicates that the residue contained 99.9 per cent. of silver. In the case of another sample of the residue prepared and analyzed in the same way, 0.04320 gram of residue yielded 0.05747 gram of silver chloride, which indicates that the residue contained 100.1 per cent. of silver. The mean of the two analyses is 100.0 per cent. of silver. These analyses prove conclusively that when silver phosphate is acted on by light in the presence of water, it is so altered (perhaps by the formation of a subphosphate similar to subchloride) that when treated with very dilute nitric acid metallic silver remains.

It does not follow, however, that it would be a correct procedure to determine the per cent. of this residue obtained from the samples used for analysis and apply a correction on the assumption that the material consisted of pure silver phosphate and a small amount of pure silver. This procedure would assume that the other product of decomposition is eliminated and not weighed. There are two facts which show that this assumption would be incorrect. In nearly every analysis, when the solution was diluted, after bringing the residue into solution by heating on the steam bath, a slight opalescence was produced. Careful tests of the water used showed that this opalescence was not due to impurity in the water. It seems probable that the substance which caused this opalescence was derived in part from the phosphate radical during the decomposition which produced the residue. The other fact is that dry silver phosphate does not lose weight when darkened by exposure to sunlight, although this treatment increases the amount of residue. The conclusion in regard to this residue may be summarized as follows: The washed moist silver phosphate was free from residue and contained silver and phosphoric acid combined in atomic proportions. During the drying and weighing a slight decomposition took place, undoubtedly owing in part at least to the action of light. It seems probable that during this decomposition no loss in weight took place, and therefore the sample contained the proper percentage of silver. When this slightly darkened silver phosphate is treated with cold, dilute nitric acid, the unchanged silver phosphate and perhaps also a portion of the altered material dissolve, leaving a slight opalescence, which in some cases is deposited as a very slight residue on standing. This residue is estimated to be about 0.01 per cent. of the weight of the silver phosphate. When the solution is warmed until perfectly clear, and then diluted, a very slight opalescence is usually produced which could be again cleared up by warming the solution. This opalescence is probably caused by the presence of the altered phosphate anion. If this explanation is correct, the presence of the residue cannot influence the result, and no correction need be applied. Until the exact nature of the decomposition products can be determined, there must remain some uncertainty in regard to whether or not any correction is necessary.

The uncertainty from this cause is, however, not very great. Even if all the phosphorus and oxygen corresponding to the residue of silver are removed before the weighing, the correction would be only 23 per cent. of the weight of the residue. If the residue amounts to 0.01 per cent., as has been estimated, the maximum correction would be 0.002 per cent. If part of the oxygen is lost, but the phosphorus remains, the correction would of course be smaller. If there is no loss in weight by the action of light on the dry silver phosphate, no correction need be applied. From the evidence so far obtained the latter assumption seems rather more probable than any of the others, and therefore no correction has been applied.

The Determination of Water in the Dried Silver Phosphate.

In order to find out how efficient the drying of the silver phosphate had been, experiments were made to determine the amount of water retained by silver phosphate which had been dried for analysis as described above (see page 308). The water was determined by fusing the dried phosphate in a current of dry air and collecting the moisture set free in a weighed phosphorus pentoxide tube. Since the melting point of pure silver phosphate is considerably above the softening point of hard glass, it was found advantageous to lower the melting point of the phosphate by the use of silver chloride as a flux.

About 15 grams of silver phosphate were placed in one end of a large silver boat and in the other end about 12 grams of previously fused silver chloride. The boat was then inserted in a hard glass tube and dried under the same conditions as prevailed in preparing the samples for the determination of the silver content. After the silver phosphate had been heated for seven hours in a current of purified air dried by phosphorus pentoxide, the air passing over the boat in the furnace was conducted through a weighed U-tube containing resublimed phosphorus pentoxide for one-half hour. This was done to make sure that all the water which had been liberated from the silver phosphate without fusion had been swept out of the apparatus. In no case was there a gain in weight during this process of more than 0.05 mg., which is about the limit of error in weighing the phosphorus pentoxide tubes. The backward diffusion of moisture was prevented by a second tube containing pentoxide.

The carefully weighed phosphorus pentoxide tube was again attached to the tube containing the silver boat with its charge of silver phosphate and silver chloride. The latter tube was then heated hot enough to fuse the silver chloride, which flowed down to the silver phosphate and readily caused the entire charge to fuse completely. The liberated water was swept into the phosphorus pentoxide tube by a current of dry air for about thirty minutes. The tube was then reweighed to determine the water evolved by the fusion of silver phosphate. The pentoxide tube was weighed by substitution for a very similar counterpoise tube, one stopcock of each tube being open during the weighing. Before being weighed both tubes were wiped with a damp cloth and allowed to stand near the balance for at least thirty minutes.

The following table gives the results of these experiments:

Sample	Weight of silver phosphate	Weight of water.	Per cent. of water.
P	13.50	0.00012	0 0009
P	15.64	0 00007	0.0004
O	15.66	0.00005	0.0003
O	16.62	0 00003	0.0002
		Average,	0.0005

The amount of water evolved is hardly greater than the probable error in weighing the phosphorus pentoxide tubes, and is less than the probable error in determining the amount of silver in the salt. We are therefore justified in concluding that the material which was used for the determination of silver was essentially free from water and that no correction need be applied to the results for inefficient drying.

This result also furnishes evidence that the samples are free from acid phosphates, which, owing to conversion into pyro- or metaphosphate, would evolve water when fused, although it is possible that occluded acid phosphates might have been converted into pyro- or metaphosphates during the drying. Sample O, which was prepared under conditions most favorable for the formation of the acid silver phosphate, does not appear to contain more water than Sample P, which was prepared under conditions which were unfavorable to the formation of acid phosphate. Since these two samples, which differed most widely in their method of preparation, showed no difference in the amount of water retained, it seemed unnecessary to test the other samples also. Unfortunately this method of detecting acid phosphate is not very sensitive, owing to the unfavorable relation of the atomic weights involved—one molecule of water corresponding to a deficiency of two atoms of silver.

The Specific Gravity of Silver Phosphates.

In order that the apparent weight of the silver phosphate might be corrected to the vacuum standard, the specific gravity of this salt was found by determining the weight of toluene displaced by a known quantity of salt. The specific gravity of the toluene at 25° referred to water at 4° was 0.8633. Great care was taken to remove air from the salt when covered with the toluene by warming the pycnometer, then placing it in a vacuum desiccator and boiling the toluene under reduced pressure. The salt and toluene were mechanically stirred to assist the escape of air bubbles. This process was repeated several times.

Weight of silver phosphate in vacuum. Grams	Weight of displaced toluene in vacuum. Grams	Volume of silver phosphate cc	Density of silver phosphate. 25°/4°.
22.955	3.113	3.606	6.366
16.942	2.205	2.658	6.374
		Mean,	6.37

Therefore the apparent weight of silver phosphate was corrected to the vacuum standard by adding 0.000044 gram per gram of salt. Similarly 0.000041 gram was added for every gram of silver bromide.

The Adsorption of Air by Silver Phosphate.

Since the silver phosphate was in a very finely divided condition and since many fine powders have the power of adsorbing appreciable quantities of air or other gases, the possibility of the adsorption of air by silver phosphate was investigated. The method of experimenting and the apparatus were very similar to that used by Baxter and Tilley for investigating the behavior of iodine pentoxide

"Two weighing bottles were constructed with long, very well ground stoppers which terminated in stopcocks through which the tubes could be exhausted. These tubes were very closely of the same weight and very nearly the same internal capacity. The tubes were first exhausted and compared in weight by substitution. Next they were filled with dry air and again weighed, the weighing being carried out with stopcocks open. Both steps were then repeated with essentially the same results."[1]

In these two experiments, when air was admitted, the counterpoise gained 0.00028 and 0.00021 gram respectively (average 0.00025) more than the tube which was later to contain the silver phosphate. After 22.69 grams of pure dry silver phosphate had been placed in the tube the tube and its counterpoise were exhausted and the difference in weight determined. When dry air at 25° and 766 mm. was admitted to both the tube containing the silver phosphate and the counterpoise, the counterpoise gained 0.00443 gram more than the tube. Therefore the air displaced by the silver phosphate was 0.00443 — 0.00025 = 0.00418 gram. Since 22.69 grams of silver phosphate of density 6.37 have a volume of 3.56 cc., the volume of pure air displaced at 25° and 766 mm. should weigh 0.00425 gram.[2]

---

[1] Baxter and Tilley, This Journal, 31, 214 (1909).

[2] Rayleigh's value for the density of air at 0° and 760 mm., 1.293 grams per liter, is used. *Proc. Roy. Soc.*, 53, 147.

The experiment was then repeated. After the air had been exhausted from the tube and its counterpoise, the tube containing the silver phosphate was heated gently. No gas was evolved. The tube and its counterpoise were then weighed by substitution. When dry air at 24.5° and 767 mm. was admitted to both, the counterpoise gained 0.00445 gram more than the tube containing the silver phosphate. Therefore the air displaced by the silver phosphate was 0.00445 — 0.00025 = 0.00420 gram, whereas the weight of air displaced, calculated from the density of the salt, is 0.00426 gram.

The agreement between the experimental results and those calculated from the density of silver phosphate on the assumption that no adsorption takes place is close enough to show that no significant amount of adsorption occurs.

Discussion of the Results.

The following table contains all of the analyses not vitiated by a known impurity in the sample or by an accident during the analysis. One feature of this table requires further explanation. In Analysis 5 the silver was determined by precipitation as chloride instead of bromide. For every gram of silver phosphate there was obtained 1.02707 grams of silver chloride. Since Baxter found AgBr : AgCl = 1.31017 : 1.00000,[1] this analysis indicates that 1 gram of Sample N is equivalent to 1.02704 × 1.31017 = 1.34560 grams of silver bromide. This result is placed in the table for comparison with the other analyses and is used in the computation of the mean.

SERIES I.

$3AgBr : Ag_3PO_4$.

Number of Analysis	Sample of Ag_3PO_4.	Weight of Ag_3PO_4 in vacuum. Grams	Weight of AgBr in vacuum. Grams.	Weight of asbestos. Gram.	Dissolved AgBr. Gram.	Loss on fusion. Gram.	Corrected weight of AgBr. Grams.	Ratio $\frac{3AgBr}{Ag_3PO_4}$.
1	O	6.20166	8 34427	0.00036	0.00034	0.00007	8.34490	1.34558
2	O	6.35722	8.55386	0.00041	0.00003	0.00011	8.55419	1.34559
3	N	5.80244	7.80792	0 00029	0.00005	0.00007	7.80819	1.34567
4	N	5.05845	6.80658	0.00019	0.00020	0.00012	6.80685	1.34564
5	N	3.34498	(AgCl) 3.43514	0.00029	0.00009	0.00008	(AgCl) 3.43544	1.34560
6	P	7.15386	9.62648	0.00046	0.00013	0.00013	9.62694	1.34570
7	P	7.20085	9.68929	0.00023	0.00005	0.00010	9.68947	1.34560
8	R	6.20182	8.34466	0.00041	0.00027	0.00012	8.34522	1.34561
9	R	5.20683	7.00543	0.00029	0.00040	0.00007	7.00605	1.34555

Average, 1.34562

Per cent. of Ag in Ag_3PO_4, 77.300

A careful study of these results shows that the composition of silver phosphate is very nearly, if not quite, independent of the changes in the acidity of the solutions from which it is precipitated. Samples O and R were prepared under slightly more acid conditions than Samples N and P. The average amount of silver bromide obtained from 1 gram of Samples O and R is 1.34558 (77.297 per cent. of silver), whereas the average from Samples N and P is 1.34564 (77.301 per cent. of silver). This difference, if real and significant, is probably due to a very slight occlusion of disilver hydrogen phosphate by samples O and R. It does not seem probable that any basic salt was present in Samples N and P, because silver shows little tendency to form basic salts and the conditions of precipitation were not favorable for the formation of basic salts.

---

[1] THIS JOURNAL, 28, 1322 (1906).

The difference between composition of the samples is so slight, both in absolute amount and by comparison with the differences between different analyses of the same sample, that in the present state of our knowledge it does not seem justifiable to reject the analyses of Samples R and O. This conclusion is supported by the fact that the water determinations failed to show a difference between these samples. The results, however, indicate that the average ratio 1.34562 (77.300 per cent. of silver) may be slightly too low, owing to the presence of disilver hydrogen phosphate. The ratio 1.34562, assuming the atomic weight of silver to be 107.88, and assuming that silver bromide contains 57.4453 per cent. of silver, leads to an atomic weight of 31.043 for phosphorus, whereas the ratio 1.34564 derived from Samples N and P gives the value 31.037. The rounded-off value, 31.04, may be considered to be essentially free from error from this source. With values for the atomic weight of silver of 107.87 and 107.86, the atomic weight of phosphorus becomes 31.03 and 31.02 respectively.

Owing to the high molecular weight of silver phosphate and to the small percentage of phosphorus, a given percentage error in determining the ratio of silver bromide to silver phosphate is multiplied over thirteen times in the atomic weight of phosphorus. Thus while the extreme values for the ratio differ by only a little over one one-hundredth of a per cent., the values for the atomic weight of phosphorus differ by fifteen hundredths of a per cent., or 0.047.

We are greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in pursuing this investigation; also to the Cyrus M. Warren Fund for Research in Harvard University for many pieces of platinum apparatus.

Summary.

1. A careful study has been made of the conditions necessary for the preparation of pure trisilver phosphate.

2. It is found that silver phosphate can be almost completely dried without fusion by heating in a current of dry air.

3. The density of silver phosphate is found to be 6.37.

4. It is found that silver phosphate does not adsorb a significant amount of air.

5. Nine analyses, made with four different samples, show that 1 gram of silver phosphate yields 1.34562 grams of silver bromide, whence the per cent. of silver in silver phosphate is 77.300.

Therefore,

If Ag = 107.88 P = 31.04
If Ag = 107.87 P = 31.03
If Ag = 107.86 P = 31.02 .

CAMBRIDGE, MASS., November 12, 1909.

THE SOLUBILITY OF GOLD IN NITRIC ACID.[1]

BY FREDERIC P DEWEY.

Received December 29, 1909

If there is any statement that is firmly established in general chemical literature it is that gold is not soluble in any single acid. In the literature of assaying, however, may be found various statements to the effect that, in parting gold from silver in assaying, gold may go into solution in the nitric acid used.

Makins[2] boiled a series of samples of parted gold in nitric acid of two different strengths and found an increasing loss of gold depending upon the amount of boiling, but he did not establish the purity of the acid used, nor the presence of gold in the acid after boiling. Neither did he determine the amount of silver remaining in his cornets.

In discussing the causes of loss of gold in making gold bullion assays, Rose[3] states that 8 per cent. of the loss is due to the gold going into solution in the nitric acid during parting. This statement is apparently based upon the author's own work, but no details are given to explain or sustain it.

Rickets and Miller[4] quote this statement from Rose without comment.

In his latest book Rose,[5] immediately after the general statement that gold is not perceptibly attacked by nitric acid, adds that finely divided gold is slightly soluble in boiling nitric acid, but gives no experimental data.

In speaking of the silver remaining in the gold after parting, Lodge[6] says, "If strong nitric acid (1.42 sp. gr.) is used this amount of silver may be slightly reduced, but the gold will begin to dissolve." However, he gives no data upon the subject.

---

[1] Presented by permission of the Director of the Mint.

[2] *Quarterly Journal Chemical Society*, 13, 99 (1861).

[3] "Metallurgy of Gold," p. 479.

[4] "Notes on Assaying," p. 129.

[5] "Precious Metals," p. 14.

[6] "Notes on Assaying," p. 144.

Hillebrand and Allen,[1] after reviewing various previous statements upon the subject, describe their own tests, which tended to show that parted gold was slightly soluble in nitric acid. Their results, however, are not conclusive, for, while we may assume that reasonable precautions were taken to insure the purity of the acid used, these precautions are not stated and, while the utmost care was taken to guard against loss by float gold, yet invisibly fine particles of gold may have been suspended in the acid. It would have been better if the solutions had been filtered before evaporation, and if the porcelain dishes containing the residue after evaporation had been gently heated with a few drops of aqua regia, and a small amount of strong hydrogen sulphide water added, and the solution filtered off before the dishes were wiped out with filter paper, adding the filter to the wiping paper before cupelling. Again, in testing the parting solutions for gold, no tests are given to show the freedom of the separated silver from gold.[2]

The chief difficulty militating against the certainty of the results in experimenting upon this subject lies in the minute quantities involved when only small quantities of gold are employed for the tests.

For a long time I have been engaged upon an extensive investigation into the accuracy of gold bullion assays. A preliminary paper giving the figures obtained in comparing many hundred assays was read at the Seventh International Congress of Applied Chemistry at London, May 27 to June 3, 1909, and at the Spokane meeting of the American Institute of Mining Engineers.[3] This paper will also be published in the forthcoming report of the Director of the Mint for the fiscal year ended June 30, 1909.

In following up this matter by an investigation into the conditions surrounding and affecting the accuracy of the work of making a gold bullion assay, the possible solubility of the gold in the nitric acid during parting becomes an important point. My preliminary results were so decisive that the work was somewhat extended and it was found easy enough to thoroughly demonstrate this solubility when large amounts of gold were employed and to dissolve finely divided gold in boiling nitric acid of 1.42 sp. gr. with only a small amount of gold.

A few tests made upon regular assay work will suffice here. The acid from parting nine fine gold assays was treated with a very small amount of hydrochloric acid, the precipitate filtered off and assayed, yielding 0.33 mg. of gold. To the filtrate a small amount of lead acetate was added and then sulphuric acid. The whole was evaporated to fumes, the residue filtered off and assayed, yielding 0.04 mg. of gold.

---

[1] Comparison of assays, "Gold Telluride Ores," *Bull.* 253, U. S. Geological Survey, p. 27.

[2] Prof. Hillebrand wishes me to state that the acid used by them was 1:1.

[3] *Bull. Am. Inst. Mining Eng.*, August, 1909, p. 705.

The acid from nine coin proof assays was allowed to stand several days, when it was filtered and the filter paper was assayed, yielding 0.29 mg. of gold. To the filtrate a small amount of hydrochloric acid was added and the precipitate assayed showing 0.02 mg. of gold. A second treatment with hydrochloric acid gave no gold.

The acid from nine coin proof assays was filtered when nearly cold and the filter yielded 0.26 mg. gold. On standing two days and filtering again 0.16 mg. of gold were recovered. Treatment of the second filtrate with a very slight amount of hydrochloric acid failed to give any more gold.

In our regular assay work we boil the cornets twice in 1 : 1 acid for 10 min. each time and then in 3 : 2 acid for 10 min. In the next test on nine coin proof assays the acids were kept separate. On filtering, when cool, not cold, Nos. 1 and 2 gave only questionable indications of gold while No. 3 yielded 0.02 mg. of gold. On standing 3$^1/_2$ days and filtering, No. 1 gave no visible gold, No. 2 only the faintest specks, while No. 3 gave 0.14 mg. of gold. On treating the filtrate with a very slight amount of hydrochloric acid, Nos. 1 and 2 gave no gold, but No. 3 gave 0.02 mg. gold. On treating the second filtrates with a small amount of hydrogen sulphide water all three samples failed to show gold.

While these results may appear to be somewhat confused, yet they show conclusively that the acid from the parting carries gold, that, while the gold is not visible, yet some of it may be removed by filtering and that even after standing and filtering again gold may still be recovered from the filtered acid.

This state of affairs might give rise to considerable speculation as to just what the action of the acid on the gold might be, but I pass to further more elaborate and more conclusive tests.

As the amounts of gold recovered in the tests upon our regular assay work were so small I prepared some special melts of metal, approaching the composition of our regular assay buttons, but containing differing proportions of silver, and loaded the parting basket in one case to its utmost capacity. The small bars were rolled out thin, with frequent annealing, cut into strips and put into the regular cups in the basket.

The first metal contained about 20 grams of gold, 46 grams of silver, a little copper and less lead. This sample was boiled three times for ten minutes each in the dilute acid and twice in the stronger acid. A total of 1.30 mg. of gold was recovered from the fifth acid. The cornets remaining after this prolonged boiling weighed 20.61 grams and contained 22.36 mg. silver.

The nitric acid used in the tests so far described was taken from the regular laboratory supply and, while I have no especial reason for doubting its integrity, for the next test the acids were especially prepared by treating a large conical flask of each strength with a little nitrate of silver and allowing them to stand at rest for over a week before using them.

The second metal consisted of 25.03 grams of cornet gold, 63.7 grams of silver, 0.125 gram copper and 0.075 gram lead. This sample was boiled four times in the dilute acid and three times in the stronger acid for varying lengths of time, and then given a fifteen-minute boil in the full strength of 1.42 sp. gr. acid. The acid from the last boil was colored distinctly yellow. After standing four days, the acid from the seventh boil, which was 15 minutes in 3 : 2 acid, was filtered and the filter showed 0.12 mg. of gold, while the filtrate showed 1.48 mg. of gold.

The gold was then boiled in a tall plain beaker in 1.42 acid from the laboratory stock for a full hour, producing about 500 cc. of a yellow solution, carrying gold at the rate of 77.2 mg. per liter.

The gold was then boiled in 1.42 acid from the laboratory stock for two hours producing about 600 cc. of a bright yellow solution, carrying gold at the rate of 183.3 mg. per liter.

The cornets remaining after this drastic treatment weighed 24.83 grams and carried 6.38 mg. of silver.

A third metal was prepared from 30 grams of cornet gold, 80 grams silver, 0.15 gram copper and 0.08 gram lead, but this was a little more than the platinum basket would hold. As this metal contained rather a large proportion of silver it was cautiously treated with the dilute (1 : 1) acid to remove the silver with only a small amount of disintegration of the gold. It was then boiled nearly an hour in the stronger (3 : 2) acid.

As a quicker and more certain precaution against the possible presence of chlorine in the nitric acid, the 1.42 acid next used was boiled in the beaker at about 120° for about two hours before the introduction of the gold, after which the boiling was continued for a trifle over three hours, producing nearly 700 cc. of a bright yellow solution, carrying gold at the rate of 186.4 mg. per liter.

The next test was made in the platinum parting apparatus. About 300 cc. of acid were boiled for an hour, the gold introduced, and the boiling continued for another hour. This solution contained 26.69 mg. of gold, or about 175 mg. per liter.

A final crucial test was carried out in the platinum parting apparatus with every possible precaution. I personally opened, with the utmost care, a fresh bottle of nitric acid of the J. T. Baker Chemical Company's make, bearing the following analysis:

Specific gravity...........	1.415–1.42
Nitric acid...............	69–70 per cent.
Sulphuric acid............	None.

Hyponitrous acid	None
Chlorine	"
Iodine	"
Iron	0.0002 per cent.
Non-volatile matter	0.001 "

Lot No. 7127.

The whole platinum boiling apparatus was thoroughly cleaned and rinsed out twice with this acid and all the acid used was poured directly from the bottle into the platinum. At no time during the test was the acid allowed to come into contact with glass after leaving the original bottle.

Some of the acid was boiled about forty-five minutes and the platinum basket containing the gold used in the previous test was soaked in this acid about two hours. About 300 cc. of the acid were boiled in the second platinum dish 45 m., when the platinum basket containing the gold was introduced and the boiling continued. As the joint between the platinum dish and the platinum cover is poor there was necessarily considerable evaporation of the acid and when the gold began to stick out of the acid the boiling was stopped, the gold having been boiled a little less than two hours.

It is estimated that the solution when cold would have been about 130 cc., but the hot solution was diluted a little, poured off from some small pieces of mechanically separated gold and allowed to stand over night. In the morning the cold solution was filtered and the filter caught 0.66 mg. of gold. The filtered solution showed 86.31 mg. of gold or at the rate of over 660 mg. per liter.

The remaining gold is still in use preparing a strong solution with a new lot of acid to be used for some stability tests. On December 27th, 25 cc. of this solution showed 4.94 mg. of gold. On January 27th, there was a slight scum of gold on the surface of the liquid of which 5 cc. showed 4.94 mg. of gold. . The final weight amounted to 28.724 grams and contained 3.06 mg. of silver, 0.29 mg. of copper and traces of lead.

As a further test, proof gold, made with great care at the Philadelphia Mint as described by McCaughey,[1] was rolled out very thin and boiled in a conical flask for five hours in previously boiled nitric acid from the freshly opened bottle of Baker's acid mentioned above. The strip exposed about seven square inches of surface to the acid. An accident caused some loss of the dissolved gold, but 11.58 mg. were recovered from the solution.

My personal opinion is that the temperature required to boil 1.42 acid (120°) has fully as much, if not more, to do with dissolving the gold than the strength of acid employed.

The method followed in determining the gold in the strong solutions consisted in evaporating to dryness, digesting gently with a little aqua regia, adding a liberal amount of strong hydrogen sulphide water, and, after gentle heating, adding some nitrate of silver solution, so that the sulphide of gold would be enclosed and protected by the sulphide of silver. The sulphides were filtered off, put into a porcelain crucible and the filter burned off carefully. The metallic sponge remaining was enclosed in a small cornucopia of sheet lead, more silver added and cupelled.

---

[1] THIS JOURNAL, 31, 1262.

After trying various methods of gathering a little gold out of a solution containing much silver, I have come to prefer strong hydrogen sulphide water as it is a most excellent precipitant for the gold and the co-precipitated silver protects the gold in the subsequent operations, which are simplified for the sulphide precipitate over a chloride of silver precipitate. In practice a limited amount of the hydrogen sulphide water is added to the solution, which is allowed to stand, with occasional stirring, a day or two, before filtering.

It is a very easy matter to exhibit the solubility of finely divided gold in strong nitric acid. By alloying a small piece of gold with $2^1/_2$–3 times its weight of silver, and dissolving out the silver in diluted nitric acid the gold will be left in good condition for such a test. Five minutes' hard boiling in a few cubic centimeters of strong nitric acid, which may have been previously boiled if desired, will give a distinctly yellow solution, which may be further tested for gold.

The discussion of the application of these results to the question of gold bullion assaying is reserved for a future paper on the general subject of the accuracy of such assaying, but I would say that the practical conclusion of Hillebrand and Allen,[1] that the solubility of the gold in the parting acid in ordinary ore assaying is negligible, is undoubtedly sound, unless the ores be most unusually rich in gold, but the excessive boiling in nitric acid sometimes used by them in their tests might dissolve an appreciable amount of gold in very rich ores and even this drastic treatment is not entirely sure to remove all of the silver, unless more than three parts of silver to one of gold were present originally.

BUREAU OF THE MINT, WASHINGTON, D C.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

HALIDE BASES OF TANTALUM.

BY WILLIAM H. CHAPIN.

Received January 17, 1910.

Preparation of a Lower Bromide of Tantalum from the Pentabromide.

While attempting to produce a lower bromide of tantalum by reduction of the pentabromide in hydrogen, Van Haagen[2] obtained a small amount of a new green compound which he found to possess very remarkable properties. It dissolved in water without decomposition, and it suffered no change even when its solution was boiled or evaporated in the open. In the solid state it was perfectly stable in the air. Moreover it possessed remarkable tinctorial powers, a few milligrams being sufficient to color several hundred cubic centimeters of water a bright emerald-green. Also a piece of silk dipped in its solution afterwards possessed a delicate green color which was not removed by washing. With ammonia the compound gave a brown hydroxide, which on exposure to the air became white. What the structure of the new bromide was Van Haagen was not able to determine because of lack of time and material, but an analysis attempted on a very small sample pointed to something approaching a tribromide.

---

[1] *Loc. cit.*

[2] Thesis, "Tantalum and Some of Its Halides," Univ. of Pa., 1909.

A few months later while engaged in the preparation of material for further investigation, we noticed the announcement of a new chloride of tantalum by Chabriè.[1] The properties of this compound, as described by its discoverer, corresponded in almost every detail with those of Van Haagen's bromide. The method of preparation, however, was entirely different, consisting essentially in the reduction of tantalum pentachloride in the dry way by means of sodium amalgam. Chabriè noted the crystalline form of his chloride, and also by means of the spectroscope proved its identity as a compound of tantalum. Owing to scarcity of material, however, he, too, gave but a single analysis; but from the results obtained believed himself justified in ascribing to the compound the formula $TaCl_22H_2O$.

A method being needed by which to prepare the bromide in larger quantity, Chabriè's announcement was welcome, and upon trial it was found that the method could be used with fair success. It finally was the only method used, although it was found to yield better results after slight modification. The following is an outline of the procedure: One part of tantalum pentabromide was mixed with four parts of 3 per cent. sodium amalgam, and the mixture quickly introduced into a combustion tube of hard glass. The air was then exhausted by means of a water pump, and the tube gradually heated, finally to redness. The reduction product was allowed to cool completely in a vacuum, and was then removed and thrown into water acidulated with hydrobromic acid. The by-products were filtered off, and the intensely green solution concentrated on the water bath until the acid present finally caused the compound to separate as a crystalline powder, leaving the supernatant liquid of a yellowish color. This powder was removed, washed with hydrobromic acid, and finally dried on a water bath.

The yield of the green bromide obtained by this method was always very slight, averaging only about 15 per cent. of the theory. Altogether 20 grams were obtained, and to do so 200 grams of the pentabromide were used. Just what this means can be appreciated by one who has made 200 grams of pure tantalum pentabromide. Fortunately the compound as first obtained was remarkably pure, and for that reason there was no necessity for repeated crystallizations and consequent loss of material.

---

[1] *Compt. rend.*, 144, 804 (1907).

The by-products mentioned above were important since they represented by far the larger part of the tantalum used. They seemed to consist of some lower oxide. While wet they were of a brown color, but upon drying became gray, and upon strong ignition they became pure white, and appeared then to be ordinary tantalum oxide. As will be shown later these by-products were turned to good account in establishing the identity of the bromide.

Some of the properties of this green bromide have already been mentioned, among them its high coloring power. As evidence of this it might be mentioned that a solution containing 1 gram per hundred cubic centimeters possessed such an intense color that a layer half an inch thick was perfectly opaque. Examined under the microscope the substance was found to consist of beautiful hexagonal crystals. No crystals over 0.25 mm. in diameter were ever seen, but they were often very brilliant, causing the powder to sparkle when placed in the sunlight. As ordinarily prepared the compound was black, but if ground down in a mortar it became dark green in color.

Identification of the Bromide as a Compound of Tantalum.

Although Chabriè had shown his chloride to be a tantalum compound it was not thought superfluous to obtain definite proof as to the identity of the new bromide. To this end the oxides mentioned above as "by-products" were collected and converted into the pentabromide. This was then reduced by means of sodium amalgam, producing a fresh yield of the green bromide, and of course more of the "by-products." The latter being collected, the process was repeated until finally the residue obtained was too small in amount to work with. If the bromide were not a tantalum compound the yield should have grown smaller each time the cycle was repeated, until finally a residue was obtained which would not respond to the reaction. No such diminution in the yield was noticed, however.

As further proof of the identity of the new bromide a portion was decomposed, and converted into the well-known double fluoride, K_2TaF_7. The product thus obtained possessed all the characteristic properties of this salt; and carefully conducted analyses failed to disclose any difference, as the following results will show:

K as K_2SO_4	Found	44.32,	Calculated	44.46 per cent.
Ta as Ta_2O_5	Found	56.40,	Calculated	56.32 per cent.

These results serve to confirm those mentioned in the last paragraph, and are to be accounted for only by assuming that we are here dealing with a tantalum compound.

Structure of the Bromide.

As has already been mentioned Chabriè regarded his compound as a dichloride, $TaCl_2 2H_2O$; and considering the close similarity of the two bodies there seemed no reason to doubt that the bromide would be found to possess an analogous structure, as represented by the formula $TaBr_2 2H_2O$. However, as the following example will show, the results of the analyses did not agree with this supposition:

	Found, per cent.	Calculated, for $TaBr_2 2H_2O$, per cent.
Ta	46.60	48.01
Br	48.06	42.44
H_2O	5.46	9.55
	100.12	100.00

The methods used for the analyses were very simple. The tantalum was precipitated from the boiling solution by means of ammonia, and subsequently ignited to the oxide Ta_2O_5. For the determination of the bromine one of two methods was employed: *first*, the filtrate from tantalum was acidified with nitric acid, and the bromine precipitated as silver bromide; or *second*, the filtrate from tantalum hydroxide was simply evaporated to dryness in a weighed porcelain crucible, and the residual ammonium bromide dried to constant weight in an oven at 100°. The results obtained by use of these two methods were surprisingly concordant, the maximum variation being less than 0.1 per cent. After the second method had been thoroughly tested it was given the preference, since its use permitted the application of a very simple check on the tantalum value. This consisted in the decomposition of the ammonium salt by means of nitric acid, and subsequent weighing of a very slight residue of oxide which had escaped the filter. It may be mentioned that this residue never in any case exceeded 0.2 mg. and in most cases was much less than this. The ammonium bromide could, of course, have been expelled simply by heating, but this procedure would almost certainly have caused the expulsion of the tantalum residue, either mechanically or otherwise. The values for tantalum as thus obtained were very concordant, the maximum variation in a series of five analyses being 0.1 per cent.

The percentage of water in the bromide was determined by mixing with litharge to retain the bromine, placing the mixture in a porcelain boat, and then heating in a combustion tube in a current of air, the water being collected in a calcium chloride tube. Three determinations made after this manner gave the following percentage: 5.40 per cent., 5.50 per cent., 5.50 per cent. or an average of 5.46 per cent. It was found impossible to determine the water without the use of the litharge, since the compound invariably broke down, giving off hydrobromic acid before all the water was expelled.

When, after repeated analyses, it was seen that the composition of the compound as first obtained did not correspond to that of dibromide it was thought that it might not be a single substance, but a mixture of two substances, for example the dibromide and the tribromide. With this in mind the whole stock of the bromide was recrystallized in such a way as to separate it into several fractions. In this way it was hoped to cause at least a partial separation of the different compounds if more than one were present. However, upon analyzing the different fractions, absolutely no difference could be detected, and the notion that the substance was not homogeneous had to be abandoned.

Accepting the results of the analysis as final, an empirical formula was calculated; thus, $Ta_6Br_{14}7H_2O$ for which the exact values would be:

	Per cent
Ta	46.58
Br	48.01
H_2O	5.41

Comparison of these values with those obtained from analysis will show a remarkably close agreement.

It scarcely seemed possible that all these fourteen atoms of bromine could exist in the same relation to the tantalum. The more likely possibility seemed to be the presence of a complex, in which a part of the bromine would be more loosely bound than the rest. To test this possibility the solution of a weighed amount of the bromide was treated with silver nitrate, the reaction being carried out in the cold to prevent decomposition. In two such determinations the percentages of bromine obtained were respectively 7.02 and 6.76, an average of 6.89. Now the total percentage of bromine corresponding to fourteen atoms was, as already shown, 48.06. Of this the above value is almost exactly one-seventh, and therefore corresponds to *two atoms*. To make the formula agree with the experimental data, then, it should be written $(Ta_6Br_{12})Br_27H_2O$. In water solution the molecule is undoubtedly divided into a positive complex ion and two negative bromine ions.

As further evidence of the nature of the bromide its molecular weight was determined both by boiling point and freezing point methods. For the boiling point method propyl alcohol (b. p. 99°) was chosen as the best available solvent. Using 1 gram of the salt in 16 grams of solvent the observed rise in two experiments was respectively 0.055 and 0.059°, corresponding to apparent molecular weights of 1800 and 1700, or an average of 1750. Now, an ordinary salt when dissolved in propyl alcohol in the proportion used in this experiment is dissociated to the extent of about 15 per cent. Allowing, then, for *15 per cent. dissociation*, an observed *molecular weight of 1750*, and *three ions* to the molecule, the true molecular weight may be calculated with a fair degree of certainty by use of the formula, $M = Mo(x(n - 1) + 1)$ where Mo = the observed molecular weight, x = the degree of dissociation, and n the number of ions per molecule, thus $M = 1750\ (0.15(3 - 1) + 1) = 2275$. The molecular weight calculated from the formula is 2332.

A freezing point determination, using water as the solvent, gave the following results: 1 gram of the salt in 16 grams of solvent gave a lowering of 0.162°, corresponding to an apparent molecular weight of 720, or about one-third the true molecular weight. This was exactly the result expected, since in water solution at the dilution here employed ordinary salts are almost completely dissociated.

Now, bringing together the facts stated in this section: Analysis has shown that the new green compound is not a dibromide, but that its different constituents are present in the proportions represented by the formula $Ta_6Br_{14}7H_2O$. The reaction with silver nitrate indicates that in water solution one-seventh of the bromine is in the ionic condition. This should be indicated by writing the formula $(Ta_6Br_{12})Br_27H_2O$. Molecular weight determinations by both freezing point and boiling point methods point to a molecule of approximately the same size as that indicated by the empirical formula. Hence it is believed that this is the true formula of the compound.

Replacement of the Ionized Bromine.

As would probably be expected it was found possible to replace the two ionized bromine atoms by other halogens, by hydroxyl, and by almost any acid radical. Replacement of bromine by hydroxyl was effected by treating a weighed amount of the salt (in solution) with just sufficient standard sodium hydroxide solution to complete the reaction:

$$(Ta_6Br_{12})Br_2 + 2NaOH = (Ta_6Br_{12})(OH)_2 + 2NaBr.$$

The hydroxide separated in crystalline form, and being only slightly soluble in water, left the solution nearly colorless. Analysis showed it to be $(Ta_6Br_{12})(OH)_210H_2O$. It was soluble in alcohol, insoluble in ether, consisted of thin hexagonal plates, and was stable in the air below 100°.

The replacement by chlorine could be brought about by dissolving the hydroxide in hydrochloric acid, but was most easily effected by simply evaporating a solution of the bromide with hydrochloric acid. The interesting point about this reaction was the fact that only two atoms of bromine were replaced, even when concentrated acid was used and the evaporation repeated four times. That the chlorine took the place of the ionized bromine was proved by the fact that treatment of the resulting mixed halide with silver nitrate or sulphate produced a precipitation of silver chloride containing no bromide. The formula of the compound, as shown by analysis, is $(Ta_6Br_{12})Cl_2 7H_2O$.

Replacement of bromine by iodine was effected by first preparing the hydroxide, and then dissolving this in hydriodic acid. Its formula is $(Ta_6Br_{12})I_2 7H_2O$.[1]

After following the bromide through these various transformations it becomes evident that a certain part of the molecule (Ta_6Br_{12}) acts like a single element or *base*, passing unchanged through a whole series of compounds. It is therefore proposed that this be given the name *bromotantalum*. The original compound $(Ta_6Br_{12})Br_2 7H_2O$ will then be called *bromotantalum bromide*, and the other compounds mentioned above will be respectively, *bromotantalum hydroxide*, *bromotantalum chloride*, and *bromotantalum iodide*.

Chabrie's Chloride.

As already mentioned the properties of Chabriè's chloride correspond very closely with those of the bromotantalum compounds. Even the crystalline form was identical. These facts made it seem highly probable that the formula should be $(Ta_6Cl_{12})Cl_2 7H_2O$ and not $TaCl_2 2H_2O$, as Chabriè writes it. Having only a very small amount of material to work with, which at the same time may not have been pure, he could easily have made such a mistake. Moreover, Chabriè determined the water in his compound by simply heating in an atmosphere of carbon dioxide, or at least he does not mention having used a retainer for the chlorine. This procedure would certainly not succeed in case of the bromide, and may account for a high value for water and a low value for chlorine.

To settle the matter we prepared the chloride according to Chabriè's method and, upon analysis, obtained the following values:

	Found, per cent.	Calculated for $(Ta_6Cl_{12})Cl_2 7H_2O$, per cent.
Ta	63.80	63.58
Cl	29.40	29.03
H_2O	7.20	7.37

Chabriè reports the following:

	Found, per cent.	Calculated from $TaCl_2 2H_2O$, per cent.
Ta	63.83	63.1
Cl	23.85	24.4
H_2O	12.22	12.5

It should be noted that his most reliable value—the value for tantalum,

---

[1] For further details regarding these mixed compounds refer to the author's thesis "Halide Bases of Tantalum," Univ. of Pa., 1909.

—agrees much more closely with the complex formula than with the simple one, and the other values can be accounted for as mentioned above. His chloride is therefore without doubt the exact analogue of the bromotantalum bromide, and should be called "chlorotantalum chloride."

UNIVERSITY OF PENNSYLVANIA.

METALLIC TITANIUM.

BY M A. HUNTER.

Received January 19, 1910.

All the earliest attempts at the preparation of metallic titanium resulted for the most part in the production of the various nitrides which from their metallic appearance were always mistaken for the metal. Thus Wollaston[1] mistook the cyanonitride which is frequently found in the slag and metal from the blast furnace for the metal. Again Berzelius[2] reduced potassium titanifluoride with potassium and obtained a black powder which on polishing showed a metallic streak. This substance was insoluble in hydrofluoric but easily soluble in a mixture of hydrofluoric and hydrochloric acids and whatever it may have been it certainly was not metallic titanium, for titanium is immediately soluble in hydrofluoric acid. Rose[3] produced a dark blue or a black powder insoluble in hydrochloric acid from the compound $TiCl_4.4NH_3$ by heating alone or by reduction with metallic sodium. This material, which he considered to be metallic titanium, is now known to be Ti_3N_4.

Wöhler[4] and Wöhler and Deville[5] in their attempts at producing the metal succeeded in all cases in obtaining the nitrides. Up to this time no analysis of the material produced by the experimenters above mentioned appears to have been made. The confusion which existed in the earlier literature with regard to the pure metal titanium and its nitrides is therefore easily explained.

Nilson and Petersson[6] attempted to prepare metallic titanium by reducing $TiCl_4$ with sodium in an air-tight cylinder of solid steel. The metal was obtained in yellow scales (with frequently a bluish surface color) containing about 95 per cent. of titanium, the chief impurity being the monoxide of titanium.

Then Moissan[7] by reducing titanium dioxide at the extreme temperatures of his electric furnace produced a material containing 5 per cent. of carbon. On reheating this material with titanium dioxide, the amount of carbon was reduced to 2 per cent. and the resulting product was free from nitrogen. This appears to be the nearest approach to metallic titanium which has yet been obtained.

---

[1] *Phil. Trans.*, 17, 1823.

[2] *Pogg. Ann.*, 4, 3 (1825).

[3] *Ibid.*, 16, 57.

[4] *Compt. rend.*, 29, 505 (1849).

[5] *Ibid.*, 45, 480 (1857).

[6] *Z. physik. Chem.*, 1, 25 (1887).

[7] *Compt. rend.*, 120, 290 (1895).

In the following pages each of these methods of preparation is taken up in succession and the results of many attempts to obtain the pure metal from the various compounds of titanium are set out in detail.

Reduction of the Titanifluorides by the Alkali Metals.

In searching in the first instance for materials with which to work it was evident that those substances which were most soluble in water would best suit the purpose: for these materials can be most readily removed on subsequent lixiviation. Among the double fluorides sodium titanifluoride is given by Comey as the most soluble salt and among the simple fluorides of the alkali metals potassium fluoride is deliquescent. The combination of sodium titanifluoride and metallic potassium appeared then the best to use; though, as will be shown, both potassium titanifluoride and barium titanifluoride have been used as a starting material. The sodium titanifluoride was prepared in the following way: Titanium dioxide free from iron was dissolved in hydrofluoric acid. While the liquid was still hot it was filtered from the undissolved residue and almost neutralized by a hot concentrated solution of sodium hydroxide. Sodium titanifluoride was immediately thrown out as a crystalline precipitate, which was easily filtered, then washed with water containing hydrofluoric acid and on drying and bolting was ready for reduction. A sample of K_2TiF_6 prepared in this way was analyzed and found to contain 20.4 per cent. Ti instead of the theoretical 20 per cent. The discrepancy may be due to the presence of some excess of TiF_4 in the double fluoride.

The sodium double fluoride with the potassium necessary for reduction was then placed in an iron cylinder fitted with a lid loosely screwed on. This cylinder was wound with nickel wire which served as a means of heating the cylinder, and was inserted inside a second cylinder of copper which was made perfectly air-tight.

The copper cylinder was evacuated and a current was passed through the nickel wire until the reduction had taken place. This was observed by a slight shift in a manometer attached to the apparatus. When the iron cylinder had cooled it was opened, the excess of potassium was removed by dry alcohol and the whole was then thrown into a large quantity of water. The black powder remaining after several washings was collected on a filter, washed, dried and analyzed. The first material prepared after completely drying in a vacuum caught fire within 30 seconds after being exposed to air. A second material proved to be not pyrophoric in the least degree and could be easily handled in air. An analysis gave from 0.1034 gram on oxidation, 0.1040 gram TiO_2 corresponding to 60.4 per cent. of titanium. A third reduction of Na_2TiF_6 with K on treatment with alcohol and warming with successive small quantities of water gave a material which contained 68.0 per cent. Ti. A fourth experiment carried out *in vacuo* when the conditions for reduction were well ascertained gave a material which contained 73.2 per cent. of titanium.

This represents the best material yet obtained by this method. Three reductions were made on potassium titanifluoride with potassium. The resulting materials contained 60.1, 56.0, 56.1 per cent. of titanium. Barium titanifluoride reduced with potassium gave only 49.5 per cent. of the metal.

It seems to me quite certain that the double fluorides are reduced by the alkalis *in vacuo*, but that in the subsequent removal of the alkaline fluorides, the finely divided metallic titanium is attacked by the water with the ultimate formation of the oxides TiO and TiO_2. In view of the success of a subsequent method of preparing the metal the means for the prevention of this oxidation will not be further discussed.

It remains only to be said that by the methods used by Berzelius, Wöhler and Deville I could not produce a material containing more than 73 per cent. of titanium.

Reduction of Titanium Dioxide by Carbon.

The reduction of titanium dioxide by carbon was next tried as a means of obtaining titanium. To this end the purest lampblack obtainable was taken and fired at a red heat in a gas furnace to remove hydrocarbons and this carbon was then used for the reduction. An intimate mixture of the oxide and carbon was made by grinding and bolting the materials together till the whole appeared a blue homogeneous mass.

The reductions were carried out in an Arsem vacuum furnace, the heat being continued in each experiment until the charge ceased to give off gas. The analyses show the amounts of titanium oxygen and carbon in the resulting product.

EXPERIMENT I, $TiO_2 + 2C$.

Reduction carried out at 5 kw. (1800° C.) in a carbon crucible.
Analysis of product (wt. taken 0 4615 gram):

Ti	0.3656
O	0.0320
C	0.0639

Now since oxygen remains in the mixture it may be safely assumed that the carbon remaining is not in its original free condition but exists in combination with Ti and is not available for reduction. If we assume that it exists as carbide we find:

Ti combined as TiC	0.2556
Ti free or combined with O	0.1100

The ratio of Ti and O considered in atomic proportions is Ti/O = 1.14. The complete analysis of the material is then:

	Per cent.
TiC	69.2
TiO	30.8

The results are tabulated below.

Crucible.	Temp. Degrees.	Per cent. C	Ratio. Ti/O	Per cent. TiC.	Per cent. TiO.
Al_2O_3	1700	10.9	....	54.5	45.5
Carbon	1800	13.8	1.14	69.2	30.8
Carbon	1800	12.7	0 97	63.1	36.9
Carbon	2400	8.7	1.00	43.5	56.5
Carbon	2400	6 6	1 28	26.6	73.4
Tungsten	2100	4 7	....	23 6	76.4
Tungsten	2400	4 6	1.09	24.7	75.3

In general the presence of a crucible made of a substance other than carbon reduces the amount of carbon in the material but the results are largely influenced by difference of temperature during the reduction. The best results were obtained in a tungsten crucible at 2400° where the percentage of carbon remaining in the material sank as low as 4.6 per cent.

But it seems doubtful whether we can prepare metallic titanium by this method. All experiments up to this point have succeeded in giving us only a bluish purple material which contains varying quantities of TiC and TiO.

The Reduction of Titanium Tetrachloride with Sodium.

The best material which Nilson and Petersson[1] prepared by this method contained about 94.73 per cent. of titanium. The material was obtained in yellow scales (frequently with bluish surface color), the chief impurity being considered as oxygen in combination. It is quite probable that the oxygen is combined as TiO in which case the material produced would contain only 78.92 per cent. of metallic titanium.

In repeating the experiment extraordinary care was exercised during and after the reduction of the chloride by sodium to exclude air from the apparatus.

The preparation of titanium chloride was carried out on an extensive scale by the chlorination of approximately pure titanium carbide. The chloride was refluxed in a current of nitrogen to remove chlorine and then repeatedly distilled, the end fractions being continually rejected. The fraction boiling between 136° and 137° was taken and shaken repeatedly with mercury and sodium amalgam. On redistillation a perfectly water white $TiCl_4$ was obtained boiling at constant temperature (136.5° uncorrected).

---

[1] *Loc. cit.*

The first bomb used for the reduction was of 100 cc. capacity accommodating 50 grams of titanium tetrachloride and 25 grams of sodium needed for its reduction. On heating the bomb to a low red heat the reaction took place and on opening it, the titanium was found for the most part as a gray powder, some of it, however, being melted by the heat of the reaction to small metallic beads. By this means however, only 12 grams of metal were obtained in each experiment.

When the progress of the reaction was understood from this experiment on a small scale a larger bomb was constructed of ten times the capacity of the preceding one. In this bomb 500 grams of titanium chloride were successfully reduced by 245 grams of sodium, giving as a theoretical yield 126 grams of titanium. The bomb was constructed of machine steel and was capable of withstanding a total internal pressure of 80,000 pounds. The lid was screwed to the body of the bomb by six stout braces (one inch thick) screwed tightly down with an intervening gasket of soft, annealed copper.

The reaction inside the bomb must be almost instantaneous. The lid is raised a little by the force of the explosion, a slight puff of vapor escapes but the main force of the explosion is already spent and the lid closes air-tight again.

On cooling the bomb and leaching the contents with water, titanium alone remains. Thus in one experiment the weight of $TiCl_4$ used was 470 grams, the titanium content of which is 119 grams. The resultant product contained:

	Grams.
Melted metal	71
Coarse and semimolten powder	31.5
Fine powder	4.5
Total	107

The actual yield was then 90 per cent. The reaction heat had been so great that the greater part of the metal had been more or less perfectly melted during the reaction. The loss of material, amounting to 10 per cent., is accounted for by the fact that some of the titanium is oxidized during the reaction from the presence of oxygen in the sodium used. This introduction of oxygen could not be avoided even when the sodium was carefully peeled before being introduced into the reaction bomb. Again some of the finely divided metal is oxidized by the water during the washing. A flocculent blue ppt. of meta-titanic acid, which rapidly turns white in air, is formed but may be easily removed by decantation from the heavier metal beneath. The slag from the reaction, which should be pure white, is always colored blue or green from the presence of lower titanates of sodium.

This method then is an admirable one for producing titanium in moderately large quantities in a state of purity which has hitherto not been attained.

Analysis of the Material.

A bead of metallic titanium was taken, broken up in three portions and analyzed in the following ways:

1. Dissolved by long boiling in moderately concentrated hydrochloric acid—oxidized with a drop of nitric acid and the titanium precipitated with a slight excess of ammonium hydroxide.

0.1581 gram gave 0.2361 gram TiO_2 equivalent to 0.1579 gram Ti.
Per cent. titanium = 99.9.

2. Dissolved in hydrofluoric acid—neutralized and precipitated with ammonium hydroxide.

0.4365 gram gave 0.7085 gram TiO_2 equivalent to 0.4251 gram Ti.
Per cent. Ti = 97.4.

3. Dissolved in hydrofluoric acid, sulphuric acid added and the solution evaporated to the fuming point, taken up with water and precipitated with ammonium hydroxide.

0.4955 gram gave 0.7954 gram TiO_2 equivalent to 0.4773 gram Ti.
Per cent. Ti = 96.3.

The solution of the metal in hydrofluoric acid always brings about a loss of material due perhaps to the evaporation of titanium fluoride.

4. A fourth method of analysis by the solution of the metal in acid potassium sulphate and subsequent precipitation by boiling the solution gave in the hands of Prof. Mixter[1] 100.2 per cent. of titanium.

No trace of iron or of sodium could be found in the beads of titanium which were melted during the reduction and since two reliable methods of analysis yield results so closely approximating to 100 per cent. There is strong reason to believe that the material thus obtained is pure metallic titanium.

Properties of the Metal.

The metal does not differ in outward appearance from polished steel. It is, however, hard and brittle in the cold. If it be raised to a low red heat it may be readily forged like red hot iron. By this means some of the beads of from 10 to 12 grams in weight have been forged into rods about six inches long.

Unsuccessful attempts have been made to draw the material through a heated draw plate in order to produce wire from it.

The pure metal can be melted only with difficulty. A rod of metal 12 cm. long and 1.8 mm. in diameter burned in air at a temp. of 1200° when a current of 50 amps. was sent through it. The heat of oxidation was sufficient to melt the oxide thus produced. The metal was melted in a lime crucible placed in a vertical carbon tube furnace through which

[1] *Am. J. Sci.*, 27, 393 (1909).

a rapid stream of hydrogen was passed to prevent access of carbon monoxide to the metal. The resulting bead swelled up and became porous in texture resembling titanium carbide. In the Arsem furnace the resulting material was always porous and contained titanium carbide.

A rough determination of the melting point of the material was carried out as follows: The filament of a Gem incandescent lamp was superimposed on a rod of titanium maintained in as perfect a vacuum as could be obtained by a hammering Boltwood pump.

An increasing current was sent through the titanium rod and the temp. of the Gem filament was gradually raised to an equal intensity. It was found that the titanium rod slowly melted and finally broke when the Gem lamp was burning at an efficiency of 3.55 watts per c. p. The melting temperature is therefore between 1800 and 1850° and is certainly not greater than this latter value. Observations, confirming this result, were also made with a Wanner pyrometer.

The specific gravity of the metal is 4.50. It is therefore appreciably lighter than the metal obtained by Moissan (sp. gr. 4.87).

In conclusion it may be said that the metal titanium is not by any means as refractory a substance as former experimenters have been led to believe. Its melting point is comparatively low—being within one hundred degrees of platinum. Further, though brittle in large pieces in the cold yet at a low red heat it shows a remarkable malleability, and very small beads even in the cold may be flattened out with ease without disruption. A method is here given by means of which moderately large quantities of pure titanium may be produced with ease, so that the air of mystery which has so long enshrouded this refractory element will soon be dispelled.

My thanks are due to Dr. W. R. Whitney, of the General Electric Co., for suggestions and generous sympathy during the progress of this research.

Dept of Physics and Electrochemistry,
Rensselaer Poly Inst., Troy, N Y

NOTE.

The Preparation of Platinum Black.—Of the various methods which have been proposed for the preparation of the finely divided form of platinum known as "platinum black," but two are ordinarily employed, *viz.*, (1) the reduction of a solution of chloroplatinic acid by zinc, and (2) the method of Loew[1] depending on the precipitation of the platinum by means of sodium hydroxide and formaldehyde. In their study of the reducing action of platinum black on nitrates in the presence of formaldehyde, Kastle and Elvove[1] came to the conclusion that platinum black precipitated by means of zinc contains an appreciable amount of the latter metal, the presence of which influences the properties of the black to a greater or less extent, and that this zinc is ordinarily difficult of removal.

---

[1] Loew, *Ber.*, 23, 289 (1890).

It occurred to me that aluminium would be a good metal to use in place of zinc for the production of platinum black, and after a few preliminary experiments, a quantity of black was precipitated by this metal and some of the properties of this preparation investigated.

To prepare this black an aqueous solution of chloroplatinic acid containing 0.5 gram of $PtCl_4$ in 10 cc. is precipitated by the addition of an excess of commercial sheet aluminium. The action is very rapid and generates a great deal of heat. Sufficient strong hydrochloric acid is then added to dissolve any excess of aluminium. When the action is over, the solution presents the uniform black appearance of a strong colloidal solution of platinum, and at the surface of the liquid a platinum mirror is often precipitated on the walls of the container. In this condition, the platinum black will take a long time to settle out, but if the liquid is heated on a steam bath, the black will settle in minute flakes within a couple of hours. The supernatant liquid is usually yellow or greenish, probably from the presence of iron in the aluminium. This liquid is removed by decantation, and the black twice heated for one hour at 100° with fresh quantities of strong hydrochloric acid, which will remove practically all remaining metallic impurities. It is then washed with distilled water by decantation until the wash water gives no test for chlorine with silver nitrate. washed into a small beaker with distilled water, allowed to settle, the excess of water removed by decantation or with a pipette, and the black dried in a vacuum over sulphuric acid, to avoid heating.

The platinum black thus obtained is of a uniform dull black color, and between the fingers reduces to an absolutely impalpable powder. It appears to have a very considerable catalytic power, although quantitative studies of this power were not made at this time.

On analysis, the black thus prepared was found to contain 96.5 per cent. of metallic platinum. In the preliminary experiments, commercial aluminium bronze powder was used as the precipitant, but the black thus obtained was found to be contaminated with a dark brown, amorphous powder of much less specific gravity than the black. This appeared to be a mixture of organic matter and amorphous silicon. With the sheet aluminium the appearance of this contamination was not noted. From the formation of the platinum mirror, it would seem that during the process of precipitation the platinum may actually be in the colloidal state for a brief time. This mirror formation has also been noted in the reduction by formaldehyde (Loew's method), and in the reduction with sodium formate. Magnesium and iron also give very finely divided precipitates of platinum black, but the action does not appear to be so violent as with aluminium, and the blacks obtained are denser and more coherent. That from iron appeared to be badly contaminated with carbon, even though a so-called pure iron wire was used. No analysis of it was made.

---

[1] Kastle and Elvove, *Am. Chem. J.*, 31, 633 (1904).

When heated in the air the following effect upon the weight of the platinum black prepared by precipitation with aluminium was observed: Weight before heating, 0.2661 gram; weight after heating to 300°, 0.2657 gram; weight after heating to redness, 0.2630 gram; or a total loss on heating to redness of about 1.2 per cent., probably representing carbon in the aluminium. Other specimens gave similar figures.

It was also observed that while the platinum black prepared by the use of zinc becomes the gray, "spongy" platinum upon being heated to redness, that precipitated by means of aluminium changes but slightly in color, although it becomes somewhat more coherent.

It therefore appears that by this method one may obtain a quite pure, finely divided platinum black, which will prove useful where this preparation is needed in chemical work.

F. Alex. McDermott.

Hygienic Laboratory, P. H. and M. H. S., Washington, D. C.

[Contribution from the Bureau of Chemistry, U. S. Dept. of Agriculture.]

A RELATION BETWEEN THE CHEMICAL CONSTITUTION AND THE OPTICAL ROTATORY POWER OF THE SUGAR LACTONES.[1]

By C. S. Hudson

Received January 7, 1910.

The Hypothesis.

The numerous sugars are strongly rotatory. On the other hand the alcohols which result from their reduction and the acids which are formed by their oxidation are only feebly rotatory; but the glucosidic compounds of the sugars and the lactones of these acids are as strongly rotatory as the sugars themselves. Thus for example the specific rotations of the two forms of glucose are 109° and 20°, of the methyl glucosides 157° and —32°, of gluconic acid lactone 68°, but the rotation of gluconic acid is only —2°, and sorbitol, which is the alcohol that results from the reduction of glucose, shows no rotation. Is there any other property of these substances which varies in the same manner as the rotatory power?

The constitutional chemical formulas now in use for these compounds have been chosen step by step to express their chemical reactivities;

---

[1] Read at the Boston meeting of the American Chemical Society, Dec., 1909.

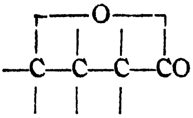
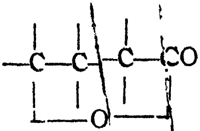
and it is now generally agreed that the sugars, the glucosides and the lactones possess a lactonic ring, but that this is absent from the structure of the alcohols and acids. Here then is a property—the chemical constitution—which runs exactly parallel with the physical property of optical rotation, in the case of the sugar glucose. Does the same parallelism hold for the other sugars?

To answer this question reference may be made to Table I, which gives the specific rotations of the principal aldose sugars, and their glucosidic, lactonic, acidic, and alcoholic derivatives, so far as they are known; the numerical values are in all cases quoted from the literature.

TABLE I.—SPECIFIC ROTATIONS OF ALDOSE SUGAR DERIVATIVES.

Sugar.		Glucosidic compound		Lactone.		Acid.	Alcohol.	
d-Glucose	α 109° β 52°	Methyl	α 157° β −32°	Gluconic	68°	−2°	Sorbitol	0
d-Galactose	α 140° β 53°	Methyl	α 196° β 0°	Galactonic	−72°	−11°	Dulcitol	0
l-Arabinose	α 76° β 184°	Benzyl	215°	Arabonic	−74°	−8°	Arabitol	0
d-Mannose	α 76° β −14°	Methyl	−79°	Mannonic	54°	?	Mannitol	0
d-Xylose	α 100° β −8°	Methyl	α 152° β −66°	Xylonic	83°	−7°	Xylitol	0
l-Rhamnose	α <−7° β > 31°	Methyl	−62°	Rhamnonic	−35°	−8°	Rhamnitol	11°
l-Ribose	?	?		Ribonic	−18°	?	Adonitol	0
d-Mannoheptose	85°	?		Mannoheptonic	−74°	?	Mannoheptitol	−1°
Rhodeose	86°	Ethyl	30°	Rhodeonic	−76°	?	?	
d-Talose	?	?		Talonic	—(strong)	?	Talitol	0.2°
d-Gulose	?	?		Gulonic	−55°	?	Sorbitol	0
α-Galaheptose	?	?		α-Galaheptonic	−52°	?	α-Galaheptitol	0
β-Galaheptose	−22°	?		β-Galaheptonic	?	?	?	
α-Gluco-octose	−51°	?		α-Gluco-octonic	46	?	α-Gluco-octitol	2°
d-Mannononose	50°	?		d-Mannonononic	−41°	?	?	
d-Gala-octose	−40°	?		d-Gala-octonic	64°	?	?	

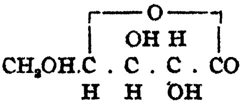
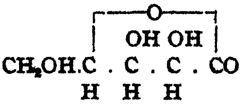
The above data from the literature show that the sugars, the glucosidic compounds and the lactones, all of which contain the lactonic ring, have strong rotatory powers. There are three apparent exceptions, β-methyl galactoside, β-xylose and α-rhamnose, but for each of these the corresponding α or β isomer is strongly rotatory, proving that the slight rotations of the three compounds are due to internal compensations, and that they contain strongly active carbon atoms. On the other hand the alcohols and acids are of feeble rotatory powers, which are in general not comparable with the strong rotations of the sugars, glucosidic compounds and lactones. There is thus satisfactory proof that the lactonic ring structure causes a strong rotatory power.

The rotations of the alcohols and acids recorded are so small in comparison with those of the lactones that the rotations of the latter may be assumed to be due, as a first approximation, entirely to the lactonic ring. There are two possible stereo structures for the lactonic ring, namely  and , which are mirror images (with the mirror placed horizontally).[1] If the rotation of the lactone is due entirely to this ring the position of the ring must determine the sign of the rotation of the lactone. The position of the ring is determined by the position which the OH group had on the γ-carbon atom before the ring was formed. These ideas thus lead to the following hypothesis: *Lactones of dextrorotation have the lactonic ring on one side of the structure, lactones of levorotation have it on the other and the position of the ring shows the former position of the OH group on the γ-carbon atom.*

Test of the Hypothesis.

This hypothesis will now be tested. In Table II there are collected the structural formulas and specific rotations of twenty-four lactones of the monobasic sugar acids, including every such lactone for which the structure and specific rotation have been determined. The first column gives the name and the second the stereo configuration of the lactone, the discovery of which is due in all cases to the immortal researches of Emil Fischer. In the third column is the statement, for convenience, of the position of the lactonic ring, whether "above" or "below" the chain, and in column four are the specific rotations of the lactones, which are quoted from the references given in the foot-notes. In most cases they were measured by Emil Fischer or his students.

TABLE II.—PARALLELISM BETWEEN THE SIGN OF THE ROTATION AND THE CONFIGURATION OF THE SUGAR LACTONES.

Lactone.	Fischer's configuration.	Ring position	Specific rotation.
l-Arabonic	 $\mathrm{CH_2OH.C\ .\ C\ .\ C\ .\ CO}$	Above	—74°[2]
l-Ribonic	 $\mathrm{CH_2OH.C\ .\ C\ .\ C\ .\ CO}$	Above	—18°[3]

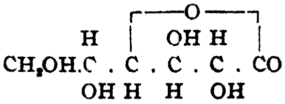
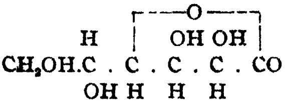
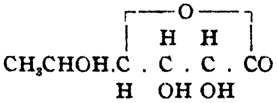
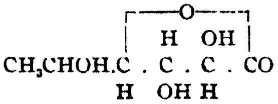
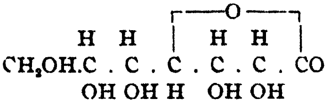
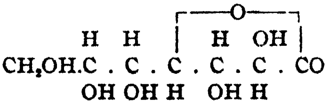
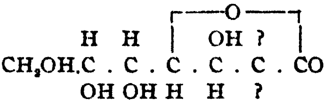
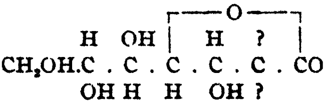
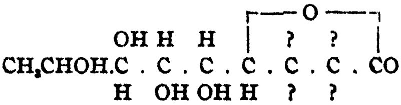
---

[1] The stereo formulas will be written horizontally to save space.

[2] E. Fischer and Piloty, *Ber.*, 24, 4219 (1891).

[3] *Ibid.*, 24, 4217 (1891).

TABLE II—(*Continued*).

Lactone.	Fischer's configuration.	Ring position.	Specific rotation.
d-Galactonic	 $CH_2OH.\underset{OH}{\overset{H}{C}}.\underset{H}{C}.\underset{H}{\overset{OH}{C}}.\underset{OH}{\overset{H}{C}}.CO$	Above	—78°[1]
d-Talonic	 $CH_2OH.\underset{OH}{\overset{H}{C}}.\underset{H}{C}.\underset{H}{\overset{OH}{C}}.\underset{H}{\overset{OH}{C}}.CO$	Above	—?[2] (large)
l-Rhamnonic	 $CH_3CHOH.\underset{H}{C}.\underset{OH}{\overset{H}{C}}.\underset{OH}{\overset{H}{C}}.CO$	Above	—39°[3]
l-Isorhamnonic	 $CH_3CHOH.\underset{H}{C}.\underset{OH}{\overset{H}{C}}.\underset{H}{\overset{OH}{C}}.CO$	Above	—62°[4]
d-α-Glucoheptonic	 $CH_2OH.\underset{OH}{\overset{H}{C}}.\underset{OH}{\overset{H}{C}}.\underset{H}{C}.\underset{OH}{\overset{H}{C}}.\underset{OH}{\overset{H}{C}}.CO$	Above	—55°[5]
d-β-Glucoheptonic	 $CH_2OH.\underset{OH}{\overset{H}{C}}.\underset{OH}{\overset{H}{C}}.\underset{H}{C}.\underset{OH}{\overset{H}{C}}.\underset{H}{\overset{OH}{C}}.CO$	Above	—68°[6]
d-Mannoheptonic	 $CH_2OH.\underset{OH}{\overset{H}{C}}.\underset{OH}{\overset{H}{C}}.\underset{H}{C}.\underset{H}{\overset{OH}{C}}.\underset{?}{\overset{?}{C}}.CO$	Above	—74°[7]
d-Galaheptonic	 $CH_2OH.\underset{OH}{\overset{H}{C}}.\underset{H}{\overset{OH}{C}}.\underset{H}{C}.\underset{OH}{\overset{H}{C}}.\underset{?}{\overset{?}{C}}.CO$	Above	—52°[8]
l-Rhamno-octonic	 $CH_3CHOH.\underset{H}{\overset{OH}{C}}.\underset{OH}{\overset{H}{C}}.\underset{OH}{\overset{H}{C}}.\underset{H}{C}.\underset{?}{\overset{?}{C}}.\underset{?}{\overset{?}{C}}.CO$	Above	—51°[9]

[1] Ruff and Franz, *Ber.*, 35, 948 (1902).

[2] E. Fischer, *Ibid.*, 24, 3624 (1891).

[3] Rayman, *Ibid.*, 21, 2048 (1888).

[4] E. Fischer and Herborn, *Ibid.*, 29, 1964 (1891).

[5] Kiliani, *Ibid.*, 19, 770 (1886).

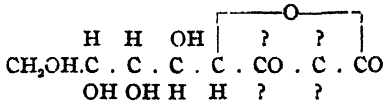
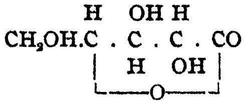
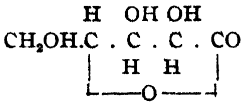
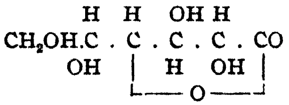
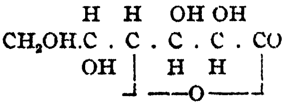
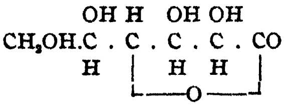
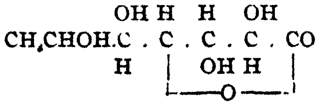
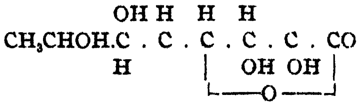
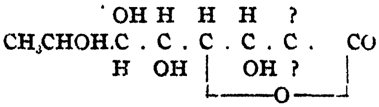
[6] E. Fischer, *Ann.*, 270, 85 (1892).

[7] E. Fischer and Passmore, *Ber.*, 23, 2228.

[8] E. Fischer, *Ann.*, 288, 143 (1895).

[9] E. Fischer and Piloty, *Ber.*, 23, 3109 (1890).

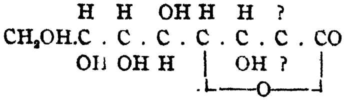
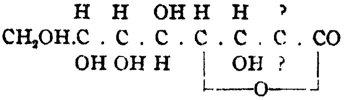
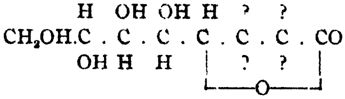
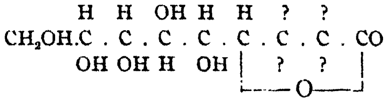
TABLE II—(*Continued*).

Lactone.	Fischer's configuration.	Ring position.	Specific rotation.
d-Manno-octonic	 $CH_2OH.\underset{OH}{\overset{H}{C}} . \underset{OH}{\overset{H}{C}} . \underset{H}{\overset{OH}{C}} . \underset{H}{C} . \underset{?}{CO} . \underset{?}{\overset{?}{C}} . CO$	Above	—44°[1]
d-Xylonic	 $CH_2OH.\overset{H}{C} . \underset{H}{\overset{OH}{C}} . \underset{OH}{\overset{H}{C}} . CO$	Below	+83°[2]
d-Lyxonic	 $CH_2OH.\overset{H}{C} . \underset{H}{\overset{OH}{C}} . \underset{H}{\overset{OH}{C}} . CO$	Below	+82°[3]
d-Gluconic	 $CH_2OH.\underset{OH}{\overset{H}{C}} . \overset{H}{C} . \underset{H}{\overset{OH}{C}} . \underset{OH}{\overset{H}{C}} . CO$	Below	+68°[4]
d-Mannonic	 $CH_2OH.\underset{OH}{\overset{H}{C}} . \overset{H}{C} . \underset{H}{\overset{OH}{C}} . \underset{H}{\overset{OH}{C}} . CO$	Below	+54°[5]
l-Gulonic	 $CH_2OH.\underset{H}{\overset{OH}{C}} . \overset{H}{C} . \underset{H}{\overset{OH}{C}} . \underset{H}{\overset{OH}{C}} . CO$	Below	+56°[6]
l-α-Rhamnohexonic	 $CH_3CHOH.\underset{H}{\overset{OH}{C}} . \overset{H}{C} . \underset{OH}{\overset{H}{C}} . \underset{H}{\overset{OH}{C}} . CO$	Below	+84°[7]
l-β-Rhamnohexonic	 $CH_3CHOH.\underset{H}{\overset{OH}{C}} . \overset{H}{C} . \overset{H}{C} . \underset{OH}{\overset{H}{C}} . \underset{OH}{C} . CO$	Below	+43°[8]
l-α-Rhamnoheptonic	 $CH_3CHOH.\underset{H}{\overset{OH}{C}} . \underset{OH}{\overset{H}{C}} . \overset{H}{C} . \underset{OH}{\overset{H}{C}} . \underset{?}{\overset{?}{C}} . CO$	Below	+56[9]

---

[1] Fischer and Passmore, *Ber.*, 23, 2234 (1890).
[2] Tollens and Weber, *Z. Ver. Zuckerind*, 49, 953.
[3] E. Fischer and Bromberg, *Ber.*, 29, 583 (1896).
[4] Schnelle and Tollens, *Ann.*, 271, 74.
[5] Fischer and Hirschberger, *Ber.*, 22, 3222 (1889).
[6] Thierfelder, *Z. physiol. Chem.*, 15, 75 (1891); E. Fischer, *Ber.*, 24, 526 (1891).
[7] E. Fischer and Piloty, *Ber.*, 23, 3104 (1890).
[8] E. Fischer and Morrell, *Ibid.*, 27, 389 (1894).
[9] E. Fischer and Piloty, *Ibid.*, 23, 3107 (1890).

TABLE II—(*Continued*).

Lactone.	Fischer's configuration.	Ring position.	Specific rotation.
d-α-Gluco-octonic	 $CH_2OH.\overset{H}{\underset{OH}{C}}.\overset{H}{\underset{OH}{C}}.\overset{OH}{\underset{H}{C}}.\overset{H}{C}.\overset{H}{\underset{OH}{C}}.\overset{?}{\underset{?}{C}}.CO$	Below	+46°[1]
d-β-Gluco-octonic	 $CH_2OH.\overset{H}{\underset{OH}{C}}.\overset{H}{\underset{OH}{C}}.\overset{OH}{\underset{H}{C}}.\overset{H}{C}.\overset{H}{\underset{OH}{C}}.\overset{?}{\underset{?}{C}}.CO$	Below	+24°[2]
d-α-Gala-octonic	 $CH_2OH.\overset{H}{\underset{OH}{C}}.\overset{OH}{\underset{H}{C}}.\overset{OH}{\underset{H}{C}}.\overset{H}{C}.\overset{?}{\underset{?}{C}}.\overset{?}{\underset{?}{C}}.CO$	Below	+64°[3]
d-α-Gluco-nononic	 $CH_2OH.\overset{H}{\underset{OH}{C}}.\overset{H}{\underset{OH}{C}}.\overset{OH}{\underset{H}{C}}.\overset{H}{\underset{OH}{C}}.\overset{H}{C}.\overset{?}{\underset{?}{C}}.\overset{?}{\underset{?}{C}}.CO$	Below	+(?)[4] (large)

The table shows that among these twenty-four sugar lactones (which include all the known substances upon which there is sufficient data known to test the hypothesis) there is not a single exception to the theory; all the lactones which have the ring "above" the chain are levorotatory and all having it "below" the chain are dextrorotatory.

Application of the Theory to Determine the Constitution of the Sugars.

As this relation between the stereo position of the lactonic ring and the sign of the rotation of the lactone is well founded it may be used in determining the constitution of the sugars. For some of the sugars such a determination is only a tracing backward of the steps of the above experimental proof of the hypothesis, but for certain others (*e. g.*, rhamnose) this method gives entirely new data on the constitution, as will be shown. In determining the constitutions of the sugars Emil Fischer has used most ingeniously a mass of chemical data of various kinds, nearly all of which he worked out in his own laboratory; in what follows it will be shown that the constitutions of the monose aldehyde sugars can be independently determined from two kinds of experimental data, (1) a knowledge of the sugars which result from the cyanide synthesis or its reverse, and (2) a knowledge of the signs of the rotations of the lactones of the monobasic sugar acids. This second kind of data cannot be obtained for the ketone sugars because they do not yield acids and lactones, and their structure cannot be found by this method alone.

---

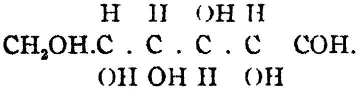
[1] E. Fischer, *Ann.*, **270**, 94 (1892)

[2] *Ibid.*, **270**, 101 (1892).

[3] *Ibid.*, **288**, 149 (1895).

[4] *Ibid.*, **270**, 103 (1892).

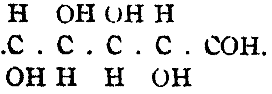
The Stereo Configuration of d-Glucose.—The cyanide synthesis or its reverse has shown the steps of the following series: *d*-erythrose ⟶ *d*-arabinose ⟶ *d*-glucose ⟶ *d*-glucoheptose ⟶ *d*-gluco-octose. The specific rotations of the lactones of the monobasic acids derived from these sugars are (see Table II), *d*-arabonic +74°, *d*-gluconic +68°, *d*-glucoheptonic —68°, *d*-gluco-octonic +46°. Writing the carbon chain of the octose $CH_2OH.\underset{(1)}{C}.\underset{(2)}{C}.\underset{(3)}{C}.\underset{(4)}{C}.\underset{(5)}{C}.\underset{(6)}{C}.\underset{(7)}{C}$, it is first noticed that as its lactone rotates positive (+46) its ring is to be considered below the chain and joining atom 7 to its γ-carbon 4. This shows that the H atom on 4 is above the chain. Passing next to the heptose, since its lactone rotates negative (—68°) the H atom on the new γ-carbon 3 by the same reasoning is below the chain. Similarly the signs of the rotations of the other two lactones show that the H atom is above 2 and above 1. This determines the stereo constitution of the carbons 1, 2, 3, and 4, and as these are all the asymmetric carbons which occur in the aldehyde formula of glucose, this may be written



$$CH_2OH.\overset{H}{\underset{OH}{C}}\ .\ \overset{H}{\underset{OH}{C}}\ .\ \overset{OH}{\underset{H}{C}}\ .\ \overset{H}{\underset{OH}{C}}\ \ COH.$$

This formula is identical with the one which Emil Fischer has chosen from chemical data alone. The steps of the above proof of the structure of *d*-glucose give also the structures of *d*-arabinose and *d*-erythrose.

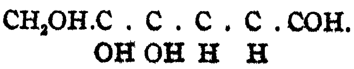
The Stereo Configuration of d-Galactose.—The cyanide synthesis or its reverse has shown the following series: *d*-lyxose ⟶ *d*-galactose ⟶ *d*-galaheptose ⟶ *d*-galaoctose, and the rotations of the lactones of the corresponding monobasic acids have been found to be (Table II) *d*-lyxonic +82°, *d*-galactonic —78°, *d*-galaheptonic −52°, *d*-galaoctonic +64°. By the same reasoning as given above these rotations show that in the stereo formula of galactose the H atom is above carbons 1 and 4 and below 2 and 3, giving



$$CH_2OH.\overset{H}{\underset{OH}{C}}\ .\ \overset{OH}{\underset{H}{C}}\ .\ \overset{OH}{\underset{H}{C}}\ .\ \overset{H}{\underset{OH}{C}}\ .\ COH.$$

This formula is identical with the one which Fischer has chosen for galactose. The stereo configuration of *d*-lyxose follows from that of *d*-galactose.

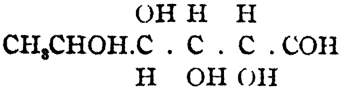
The Stereo Configuration of d-Mannose.—The cyanide reaction has shown the following series: *d*-arabinose ⟶ *d*-mannose ⟶ *d*-mannoheptose ⟶ *d*-manno-octose, and the rotations of the lactones of the corresponding monobasic acids have been found to be (Table II) *d*-arabonic +74°, *d*-mannonic +54°, *d*-mannoheptonic —74°, *d*-manno-octonic —44°. In the configuration of mannose therefore the H atom is below 3 and 4 and above 1 and 2, giving



$$CH_2OH.\overset{H}{\underset{OH}{C}}\ .\ \overset{H}{\underset{OH}{C}}\ .\ \overset{OH}{\underset{H}{C}}\ .\ \overset{OH}{\underset{H}{C}}\ .COH.$$

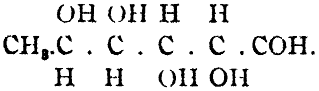
This is also identical with the structure which Fischer has established for mannose.

The Stereo Configuration of Rhamnose.—This methyl pentose sugar has been shown by Fischer to have the stereo configuration



$CH_3CHOH.\underset{H}{\overset{OH}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.COH$

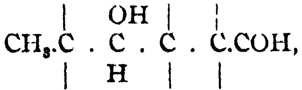
but he was unable to obtain any data which would establish the stereo structure of the first asymmetric group CH_3CHOH. This physico-chemical method for establishing the structure of the sugars can be applied in this case where the usual strictly chemical methods fail. Writing the carbon chain for rhamnose $CH_3.\underset{(1)}{C}.\underset{(2)}{C}.\underset{(3)}{C}.\underset{(4)}{C}.\underset{(5)}{C}$, and referring to the following cyanide syntheses, methyl tetrose ⟶ rhamnose ⟶ rhamnohexose ⟶ rhamnoheptose, the specific rotations of the corresponding lactones having been found to be methyl tetronic —47°,[1] rhamnonic —35°, rhamnohexonic +84°, and rhamnoheptonic +56°, it is seen that the hydrogen atom is to be placed above carbons 3 and 4 and below 1 and 2, yielding the following configuration for rhamnose,



$CH_3.\underset{H}{\overset{OH}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.\,\underset{OH}{\overset{H}{C}}\,.COH$.

This agrees with Fischer's structure for the atoms 2, 3, and 4, and it also shows the configuration of the atom 1 which has been in doubt. Rhamnose is thus a reduction product from *l*-mannose. It is interesting to note that Winther[2] has previously selected this configuration for the first carbon, basing his selection upon the fact that Tate's bacillus attacks rhamnose.

Partial Stereo Configurations of Rhodeose and Fucose.—The methyl pentose rhodeose yields a lactone with the specific rotation —76°,[3] consequently its structure can be partially determined from the above principles to be



$CH_3.\underset{|}{\overset{|}{C}}\,.\,\underset{H}{\overset{OH}{C}}\,.\,\underset{|}{\overset{|}{C}}\,.\,\underset{|}{\overset{|}{C}}.COH$,

and it follows that its antipode, fucose, is the mirror image of this.

Proof of the Position of the Lactonic Ring.

The foregoing relations furnish a proof of a view which organic chemists have been led to adopt by a large number of chemical facts, namely, that the formation of lactones involves the γ-carbon atom preferably to any other. The parallel relation between the position of the lactonic ring and the sign of the rotation of the lactone is based on the assumption that the ring is formed on the γ-carbon atom; if it were considered as formed on any other atom whatsoever the parallelism would no longer hold even approximately; thus, referring back to Table II, if the ring is supposed to form on the α-atom, there are then seven cases of agreement with the hypothesis of parallelism, eight disagreements and nine remaining doubtful. If the ring forms on the β-carbon there are then ten cases of agreement and ten of disagreement and four in doubt. If the ring forms on the δ-carbon there result six agreements, twelve disagreements and six doubtful. But it has been seen that if the ring forms on the γ-carbon there are twenty-four agreements, no disagreements and none in doubt. As the chances that an event which can happen in two equally probable ways will happen in exactly the same way twenty-four times out of twenty-four trials is only one in seventeen million it seems certain that the lactonic ring in these monobasic sugar lactones forms on the γ-carbon atom.

---

[1] Ruff and Kohn, *Ber.*, 35, 2362.

[2] *Ber.*, 28, 3000.

[3] Votocek, *Z. Zuckerind. Boh.*, 25, 297 (1902).

[Contribution from the Wellcome Chemical Research Laboratories, London.]

CHEMICAL EXAMINATION OF PUMPKIN SEED.

By Frederick B. Power and Arthur H Salway

Received January 13, 1910.

The seeds of the common pumpkin (*Cucurbita pepo*, Linné) have been recognized for several decades by the United States Pharmacopoeia under the title of *Pepo*, and are regarded as an efficient and harmless taenifuge. This property appears to have been generally attributed to the fatty oil contained in the seed, which is stated to have been used with success in repeated half-ounce doses.[1] On the other hand, Heckel[2] found that the membrane surrounding the embryo is capable of expelling tapeworms, and as the membrane contains a resin, he believed this to be the active constituent There is, however, no indication that Heckel had in any way confirmed this supposition by the separate administration of the resin. A more definite observation regarding the activity of the resin appears to have been made by Wolff, since it is recorded[3] that he found this efficient as a taenifuge in doses of 15 grams, whereas the fatty oil, when pure and free from resin, was inert. Ordinarily, however, the remedy is employed in the form of the kernels of the fresh seed, suitably prepared, in doses ranging from 30 to 200 grams.

No complete chemical examination has hitherto been made of pumpkin seeds, and the constituents of their fatty oil have been only imperfectly known. The results of an investigation by Kopylow,[4] in 1876, showed that previous statements respecting the presence of an alkaloid or glucoside in these seeds could not be confirmed, but that they contained, besides fatty oil, some sugar and a soft resin. The expressed oil was stated to consist of the glycerides of palmitic, myristic, and oleic acids, while the oil extracted from the press-cake by means of ether also contained these acids in a free state. Lewkowitsch[1] describes pumpkin seed oil, and records its physical and chemical constants, as also some of the constants of the mixed fatty acids obtained from the oil, but makes no statement concerning its composition.

---

[1] *Lancet*, Sept. 25, 1875, p. 462.

[2] *Ibid.* and *Pharm. J.*, Oct., 1875, p. 308. Compare also Vigieo, *Amer. J. Pharm.*, 1876, p. 509.

[3] *U. S. Dispensatory*, 18th Edit., p. 1012.

[4] *Pharm. Zeit. für Russland*, 1876, p. 513.

In view of the medicinal use of pumpkin seeds, and the deficiency of knowledge respecting their constituents, it seemed desirable to subject them to a complete examination. It was also thought possible that thereby, in conjunction with physiological tests, some further and more definite information might be obtained as to the character of the constituent upon which their reputed action as a taenifuge depends. The results of the present investigation, together with the conclusions drawn therefrom, are summarized at the end of this paper.

EXPERIMENTAL.

The material employed was obtained from the United States, and consisted of fresh pumpkin seeds, which corresponded in all respects to the description given of them in the United States Pharmacopoeia.

A portion of the crushed seed was first tested for the presence of an alkaloid by means of Prollius' fluid, but with a negative result.

For the purpose of a complete examination, 22.5 kilograms of the seed were crushed and the shells separated as completely as possible from the kernels. The shells amounted to 4.68 kilograms, thus corresponding to 20.8 per cent. of the weight of the seed. The ground kernels were then subjected to strong hydraulic pressure, when 4350 grams of fatty oil were obtained, corresponding to 19.3 per cent. of the weight of the entire seed. The so-called "press-cake" remaining after the removal of the oil amounted to 12.7 kilograms. These operations connected with the expression of the oil were carefully conducted for us by Messrs. Stafford, Allen & Sons, of London, to whom our thanks are due.

A portion of the entire seed, when ground and extracted in a Soxhlet, apparatus with light petroleum (b. p. 30–45°), yielded 34.3 per cent. of fatty oil.

I. Examination of the Expressed Oil.

The expressed oil of pumpkin seed, as obtained by us, when viewed in layers of moderate thickness, has a cherry-red color, and possesses a marked fluorescence, whereas in thin layers it appears greenish yellow. It is optically inactive. The constants of the oil were determined with the following results:

---

[1] "Chemical Technology and Analysis of Oils, Fats and Waxes," 3rd Edit., Vol. II, p. 509.

	Expressed oil.	Oil extracted by petroleum.
Specific gravity 20°/20°	0.9220	0.9212
Acid value	3.4	3.5
Saponification value	189.4	189.0
Iodine value	119.7	119.6

For a complete chemical examination of the oil, 250 grams of it were employed. It was first subjected to distillation with steam. The distillate contained no volatile oil and had only a very slight acid reaction, which appeared to be due to traces of acetic acid.

Hydrolysis of the Oil.

The oil which had been subjected to distillation with steam, as above described, was separated from the water, the latter then extracted with ether to recover a small amount of suspended oil, and, after adding this to the main portion, the whole was hydrolyzed by heating with an alcoholic solution of 70 grams of potassium hydroxide. The greater portion of the alcohol was then removed, water added, and the alkaline liquid repeatedly extracted with ether. The ethereal liquids were united, washed with a little water, dried with anhydrous sodium sulphate, and the ether removed, when about 1 gram of a yellow solid was obtained. On fractionally crystallizing the latter from ethyl acetate, the least soluble fraction was obtained in colorless needles, melting at 162–163°. After drying at 110° it was analyzed:

0.0698 gave 0.2139 CO_2 and 0.0749 H_2O. C = 83.6; H = 11.9.
$C_{27}H_{46}O$ requires C = 83 9; H = 11.9 per cent.

The analysis of this substance, together with the characteristic color reactions yielded by it, establishes its identity as a phytosterol.

The mother liquors from this phytosterol yielded crystalline deposits melting considerably lower than the latter, and the presence of another substance of this class, having an initial melting point of 140°, was indicated. On account of the very small amount of material it was, however, not possible to isolate the more soluble compound in a state of purity.

The Fatty Acids.

The alkaline, aqueous solution of potassium salts, which had been extracted with ether, as above described, was acidified with sulphuric acid and the liberated fatty acids taken up by ether. The ethereal solution was washed, dried, and the solvent removed, when 225 grams of total fatty acids were obtained. The constants of the mixed acids were determined in a portion from which the last traces of ether had been removed by heating for some time at 100° under diminished pressure, and were then as follows: M. p. (complete fusion), 31°; *d* 50°/50° = 0.8886; neutralization value, 199; iodine value, 123.5. Optically inactive. A determination of the acetyl value indicated the absence of hydroxy acids. No volatile acids could be detected, either in the total mixture of acids or in the aqueous liquid from which they had been removed by means of ether.

The mixed fatty acids, which consisted of a liquid and a solid portion, were first partially separated by filtration, with the aid of a pump. The solid portion, amounting to 30 grams, was fractionally crystallized from alcohol, and the fractions representing the two extremes of solubility, which melted at 57–58° and 50–54°, respectively, were analyzed.

Fraction Melting at 57–58°.—0.1290 gave 0 3561 CO_2 and 0.1463 H_2O. C = 75.3; H = 12.6.

0.1714 gave 0 4727 CO_2 and 0 1961 H_2O. C = 75.2; H = 12.7.

0.2306 neutralized 8.55 cc. 0.1 *N* KOH. Neutralization value = 208

Fraction Melting at 50–54°.—0.1800 gave 0.5003 CO_2 and 0.2048 H_2O. C = 75.8; H = 12 6.

$C_{16}H_{32}O_2$ requires C = 75 0; H = 12.5 per cent.

$C_{18}H_{30}O_2$ requires C = 76.1; H = 12.7 per cent.

These results indicated that both of the above fractions consisted of mixtures of palmitic and stearic acids. As their separation could not be effected by fractional crystallization, this was accomplished by fractionally precipitating a hot alcoholic solution of the acids with concentrated, aqueous barium acetate. Thus the fraction melting at 57–58° was converted into five fractions of barium salt, which, on treatment with hydrochloric acid, yielded acids melting at 66–67°, 64–65°, 62–63°, 59–60°, and 55–56°, respectively. Those of these fractions were analyzed:

Fraction Melting at 66–67°.—0 1247 gave 0 3474 CO_2 and 0.1440 H_2O. C = 76.0; H = 12.9.

$C_{18}H_{36}O_2$ requires C = 76.1; H = 12.7 per cent.

Fraction Melting at 59–60°.—0.1194 gave 0.3270 CO_2 and 0.1338 H_2O. C = 74.7; H = 12.5.

$C_{16}H_{32}O_2$ requires C = 75.0; H = 12.5 per cent.

Fraction Melting at 55–56°.—0.1030 gave 0 2858 CO_2 and 0.1159 H_2O. C = 75.7; H = 12.5.

This fraction was somewhat impure, and the fact that its carbon content is higher than the next preceding one, may be attributed to the presence of a little of the unsaturated acid contained in the oil.

The above results have thus afforded conclusive evidence that the solid acids consisted of a mixture of palmitic and stearic acids, the former predominating. There is, therefore, no indication of the presence of myristic acid, which has been stated[1] to be a constituent of pumpkin seed oil.

The liquid portion of the total fatty acids was neutralized with an alcoholic solution of potassium hydroxide, and subsequently an alcoholic solution of lead acetate added. The precipitated lead salt was thoroughly washed with water by decantation, and then digested with ether on a water bath. The ethereal solution, containing the lead salts of the unsaturated acids, was treated with dilute hydrochloric acid, filtered from the lead chloride, washed with water, and the ether removed. The unsaturated acids thus obtained from 250 grams of the fatty oil amounted to 140 grams, and possessed the following constants: B. p. 225–230°/12 mm.; *d* 20°/20° = 0.9009; acid value 195.3; iodine value 144.3. The product was analyzed with the following result:

---

[1] *Loc. cit.*

0.1354 gave 0.3807 CO_2 and 0.1416 H_2O. C = 76.7; H = 11.6.
$C_{18}H_{34}O_2$ requires C = 76.6; H = 21.1 per cent. Iodine value = 90.1.
$C_{18}H_{32}O_2$ requires C = 77.1; H = 11.4 per cent. Iodine value = 181.4.

It was evident from these results that the unsaturated acids also consisted of a mixture, and, in order to ascertain more definitely the nature of their constituents, a portion (36 grams) was oxidized, in alkaline solution, with an equal amount of potassium permanganate. A one per cent. solution of the latter was added gradually at the ordinary temperature, with constant stirring, and at the end of the operation sulphur dioxide was passed into the mixture until all the manganese oxide had dissolved. A pure white precipitate was thus obtained, which was separated by filtration, and digested with large quantities of ether at the ordinary temperature. The ethereal solution, after the removal of the solvent, yielded a product which, when crystallized from alcohol, separated in pearly leaflets, melting at 129–130°:

0.1240 gave 0.3093 CO_2 and 0.1276 H_2O. C = 68.0; H = 11.4.
$C_{18}H_{36}O_4$ requires C = 68.4; H = 11.4 per cent.

This product was evidently dihydroxystearic acid, and its formation proved the presence of oleic acid in the oil.

The portion of the oxidation product remaining undissolved by the above-described treatment with ether was repeatedly boiled with large quantities of water and the liquids filtered. The filtrates yielded crystalline deposits melting at about 155°. On recrystallizing these from alcohol, small leaflets were obtained which melted at 157–159°, and this melting point was not raised by fractional crystallization from either alcohol or acetic acid:

0.1470 gave 0.3314 CO_2 and 0.1365 H_2O. C = 61.5; H = 10.3.
$C_{18}H_{36}O_6$ requires C = 62.1; H = 10.3 per cent.

This substance is evidently a tetrahydroxystearic acid (sativic acid), although its melting point is lower than that usually assigned to the latter, namely 173°. It has been noted, however, by several observers that products agreeing in composition and character with tetrahydroxystearic acid possessed melting points varying from 152 to 165°, and it is therefore possible that these represent isomeric acids of the formula $C_{18}H_{36}O_6$.[1]

---

[1] Compare Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," 2nd Edit., Vol. I, p. 126, and *J. Chem. Soc.*, 87, 899 (1905).

The isolation of tetrahydroxystearic acid as one of the products of oxidation of the unsaturated acids of pumpkin seed oil is evidence of the presence in the latter of linoleic acid. As no hexahydroxystearic acid (linusic acid) could be isolated from the products of oxidation, it may be concluded that linolenic acid is not a constituent of the oil.

The portion of the precipitated lead salt which remained undissolved by the above-described treatment with ether was examined as follows: The acid was recovered and dissolved in alcohol, when by the addition of successive portions of barium acetate five fractions of barium salt were obtained The corresponding fractions of acid from these salts melted at the following temperatures: (I) 53-54°; (II) 53-54°; (III) 53-54°; (IV) 54-56°, (V) oily. After recrystallization, the melting points were as follows: (I) 56-58°; (II) 55-56°; (III) 54-55°, (IV) 57-59°. The acid values of these fractions corresponded to the following molecular weights: (I) 270; (II) 265; (III) 264; (IV) 260. The molecular weights of palmitic and stearic acids are 256 and 284 respectively. It was thus ascertained that the solid acids contained in that portion of the precipitated lead salt which was not dissolved by ether were the same as those initially separated from the total fatty acids, and consisted of a mixture of palmitic and stearic acids.

II. Examination of the Press-cake.

The so-called "press-cake," resulting from the expression of 22 5 kilograms of pumpkin seeds, deprived as completely as possible of the shells, amounted, as previously noted, to 12 7 kilograms. This material was completely extracted with hot alcohol, when, after the removal of the greater portion of the alcohol, a thin, dark-colored, oily extract was obtained, amounting to 2565 grams. The extract was brought into a flask with water and subjected to distillation with steam, but yielded no volatile product. The contents of the distillation flask separated, on cooling, into an upper layer of fatty oil (*A*) and a lower aqueous liquid (*B*), the latter containing some resin (*C*).

The Fatty Oil (A).

After separating the fatty oil as completely as possible from the aqueous liquid, the latter was extracted with light petroleum to remove a small amount of suspended oil. The petroleum liquids were then added to the main portion of oil, the whole filtered to remove suspended resin, washed with a little water, dried, and the petroleum removed. A quantity (1950 grams) of a dark green, fatty oil was thus obtained, which possessed the following constants: $d\ 20°/20° = 0.9230$; saponification value, 193.4; iodine value, 115.4. These figures are observed to be in close agreement with those afforded by the expressed oil, the complete investigation of which has already been described. It was therefore evident that this product from the press-cake merely represented that portion of the fatty oil of pumpkin seed which had not been removed by expression.

The Aqueous Liquid (B).

As the resin (*C*) contained in the aqueous liquid (*B*) was in too fine a state of division to admit of its separation by filtration, this was effected by decantation, and it was subsequently well washed with water in the same manner. The aqueous liquid (*B*) then possessed a dark brown color, and when heated with a solution of sodium hydroxide developed ammonia. It yielded a precipitate with mercuric-potassium iodide and with iodine solution, but this behavior was evidently due to protein compounds and not to the presence of an alkaloid, since a preliminary test of the powdered seed for substances of this class by means of Prollius' fluid had given a perfectly negative result.

Isolation of Salicylic Acid.

The aqueous liquid was repeatedly extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. About 1 gram of a brown, viscid mass was thus obtained, which gave, with ferric chloride a deep violet coloration. In order to purify the product it was warmed with aqueous sodium carbonate and animal charcoal, but the filtered liquid, on acidification, yielded a precipitate which could not be directly crystallized. On digesting the latter, however, with a large volume of light petroleum, filtering from the resinous matter, and removing the solvent, a very small quantity of colorless needles was obtained, which melted at 150–153°. The substance was soluble in sodium carbonate with evolution of carbon dioxide, gave a violet coloration with ferric chloride, and when heated with methyl alcohol in the presence of sulphuric acid developed the characteristic odor of methyl salicylate. Although the amount of this substance was not sufficient for an analysis, its identity as salicylic acid could be considered definitely established.

Treatment with Basic Lead Acetate.

The aqueous liquid, after extraction with ether as above described, was treated with basic lead acetate, which produced a voluminous, yellowish brown precipitate. This was collected on a filter, thoroughly washed with water, then suspended in water, and decomposed by hydrogen sulphide. On filtering the mixture a yellowish red liquid was obtained, which gave only a slight brown coloration with ferric chloride. The liquid was concentrated under diminished pressure, and, as it gave nothing crystalline on standing, was finally mixed with purified sawdust, and the dried mixture successively extracted in a Soxhlet apparatus with ether, ethyl acetate, and alcohol. These solvents, however, did not effect the separation of any crystalline substance.

The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, filtered, and this filtrate concentrated under diminished pressure. A reddish brown sirupy liquid was thus obtained, which contained a large amount of sugar, since it readily yielded *d*-phenylglucosazone, melting at 215°. The liquid deposited nothing crystalline, even on long standing, and a portion, when dried in purified sawdust and extracted successively with ether, ethyl acetate, and alcohol, likewise yielded nothing of a crystalline nature.

Treatment of the Purified Aqueous Liquid with Dilute Sulphuric Acid.

A portion of the aqueous liquid which had been purified by treatment with basic lead acetate, as above described, was heated for some time in a reflux apparatus with such an amount of sulphuric acid that the latter represented about 5 per cent. by weight of the mixture. On subsequently passing steam through the liquid, the distillate was found to contain formic and acetic acids, but no oily drops. The aqueous, acid liquid remaining in the distillation flask contained a comparatively large quantity of resin. This was collected and well washed with water, but it was quite insoluble in the usual organic solvents, and possessed no further interest. After the separation of the resin, the aqueous liquid, which had a dark brown color, was extracted many times with ether. The combined ethereal liquids were washed, dried, and the solvent removed, when about 3 grams of a yellowish brown oil were obtained, which was fractionally distilled under the ordinary pressure. A small fraction was collected at 100–120°, which contained formic and acetic acids, but the larger portion distilled between 230 and 240°. On redistilling the latter, it passed over between 240 and 260°. This oil possessed a light yellow color, was freely soluble in water, and gave a precipitate with phenylhydrazine acetate. It was, furthermore, soluble in sodium carbonate with evolution of carbon dioxide and yielded a crystalline silver salt. The latter was precipitated in two fractions by the successive addition of silver nitrate to a solution of the sodium salt, and these fractions, after drying in a vacuum over sulphuric acid, were analyzed:

I. 0.0973 of salt gave on ignition, 0.0462 Ag. Ag = 47.5.
II. 0.5404 of salt gave on ignition, 0.2628 Ag. Ag = 48.6.
$C_5H_7O_3Ag$ requires Ag = 48.4 per cent.

These results established the identity of the above-described substance as levulinic acid. Its formation may be attributed to the action of the sulphuric acid on the sugar contained in the aqueous liquid.

The aqueous liquid from which the levulinic acid had been extracted was next treated with just sufficient baryta to remove the sulphuric acid, then filtered, and the filtrate concentrated. A dark brown sirup was thus obtained, which deposited nothing crystalline on standing.

It will be seen from the above results that the purified aqueous liquid, on heating with sulphuric acid, yielded no product which would indicate the presence in it of a glucoside.

The Resin (C).

The resinous material from the "press-cake" amounted to 110 grams, and to this was added a small quantity (10 grams) of resin obtained from the shells of the seed. For the examination of this resinous material it was digested with hot alcohol, then mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 30–45°)	extracted	75.0	grams	= 62.5	per cent.
Ether	"	5 0	"	= 4.2	"
Chloroform	"	6.0	"	= 5.0	"
Ethyl acetate	"	2.2	"	= 1.8	"
Alcohol	"	16 0	"	= 13.3	"
Total,		104.2	"	= 86.8	"

By this process of extraction a portion of the resin had evidently been rendered insoluble.

Petroleum Extract of the Resin.

This was a soft, black mass. It was heated in a reflux apparatus with an excess of an alcoholic solution of potassium hydroxide, the greater portion of the alcohol then removed, water added, and the alkaline mixture extracted with ether. The ethereal liquids were washed, dried, and the solvent removed, when about 1 gram of a light yellow solid was obtained. This was crystallized a few times from a mixture of ethyl acetate and alcohol, when it finally separated in thin plates, melting at 157–159°. It was a phytosterol, and apparently identical with that previously isolated from the expressed oil of the seed.

Isolation of a New Monocarboxylic Acid, $C_{25}H_{51}O.CO_2H$.

The alkaline, aqueous liquid, from which the above-mentioned phytosterol had been separated, contained an insoluble potassium salt in suspension. This was removed by filtration and separately examined. For this purpose it was heated for some time with dilute sulphuric acid in the presence of chloroform, when a solution of the corresponding free acid in chloroform was obtained. This solution was washed, dried, and the solvent removed, when it yielded about 0.5 gram of a solid, wax-like substance. The latter was twice crystallized from alcohol, when it melted at 99°.

0.0986 gave 0.2728 CO_2 and 0 1138 H_2O. C = 75.5; H = 12.8.
0.0777 neutralized 1.65 cc. 0.1 *N* KOH Neutralization value = 119.1.
$C_{26}H_{52}O_3$ requires C = 75.7; H = 12 6 per cent. Neutralization value = 136 1.

The composition of this substance would thus appear to be represented by the formula $C_{26}H_{52}O_3$, which is that of a hydroxycerotic acid. Two hydroxycerotic acids have hitherto been recorded, one of which was obtained synthetically and is stated to melt at 86 5°,[1] while the other, calculated for the formula $C_{27}H_{54}O_3$, was isolated from coca leaves, and is stated to melt at 82°.[2] As the above-described acid melts at a considerably higher temperature than either of the acids noted, it is apparently identical with neither of them, and may possibly represent one of the numerous isomerides.

The acid, $C_{26}H_{52}O_3$, is very sparingly soluble in light petroleum and in cold alcohol, but is moderately soluble in hot alcohol, and dissolves more readily in ethyl acetate. When heated with ethyl alcohol in the presence of concentrated sulphuric acid, it yielded an *ethyl ester*, which melted at 61°. An attempt to obtain an acetyl derivative of the acid was not successful.

The *alkaline, aqueous liquid* from which the insoluble potassium salt had been removed, as above described, was acidified with sulphuric acid and distilled with steam, but no volatile acid was found in the distillate. The contents of the distillation flask were then extracted with ether, the ethereal liquid being filtered to remove some suspended resin, washed, dried, and the solvent removed. A quantity of dark colored, solid fatty acid was thus obtained which, when distilled under diminished pressure, passed over almost entirely between 228 and 233°/15 mm., only a small amount of non-volatile resin remaining behind. The distillate was crystallized from acetic acid, when a product was obtained which melted at 54°.

0.2224 neutralized 8 05 cc. 0 1 *N* KOH. Neutralization value = 203.1.
$C_{16}H_{32}O_2$ requires a neutralization value of 219.1
$C_{18}H_{36}O_2$ requires a neutralization value of 197.5.

This product evidently consisted of a mixture of palmitic and stearic acids.

The mother-liquors remaining from the crystallization of the above product were found to contain some unsaturated acid. The acids contained in the mixture were therefore evidently the same as those previously identified by us in the expressed oil of pumpkin seed.

Ether Extract of the Resin.

This was a black, soft solid, amounting to only 5 grams. It was redissolved in ether, the ethereal solution being then extracted with aqueous sodium carbonate, and subsequently with a 10 per cent. solution of sodium hydroxide. The sodium carbonate extract had a dark brown color and contained some insoluble sodium salt in suspension. The whole was acidified with dilute sulphuric acid, and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A dark brown solid was thus obtained, which was dissolved in alcohol, and the solution decolorized by animal charcoal. On concentrating the liquid a very small amount of a colorless substance was deposited, which melted at 98–99° and was identical with the acid $C_{20}H_{32}O_3$, which had previously been isolated from the petroleum extract of the resin. The subsequent extraction of the original ethereal solution with sodium hydroxide yielded only a trace of an amorphous, yellow solid, and on finally removing the ether only a small quantity of a light green, gelatinous mass was obtained.

---

[1] *Ann. chim. phys.* [7], 7, 227.
[2] *Ann.*, 271, 222 (1892).

Chloroform, Ethyl Acetate and Alcohol Extracts of the Resin.

These were all black, brittle solids, and nothing crystalline could be obtained from them.

III. Examination of the Shells.

The shells or husks from 22.5 kilograms of pumpkin seed amounted to 4680 grams, thus corresponding to 20.8 per cent. of the weight of the latter.

The material was ground and extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol there remained a dark-colored oil. This was mixed with water and distilled with steam, but no volatile product was obtained. The contents of the distillation flask separated, on cooling, into an upper layer of fatty oil (*A*) and a lower aqueous liquid (*B*), the latter containing some resin (*C*).

The Fatty Oil (A).

The entire liquid contained in the distillation flask, consisting, as above described, of fatty oil and a lower aqueous portion, was shaken with light petroleum. The petroleum liquid was filtered to remove a small amount of resin, washed with water, dried with anhydrous sodium sulphate, and the solvent removed. A quantity (595 grams) of a dark green, fatty oil was thus obtained, which possessed the following constants: $d\ 20°/20° = 0.9236$; saponification value, 190.3; iodine value, 118.5. These figures are in close agreement with those afforded by both the expressed oil and that obtained from the "press-cake," and the constituents of the three oils were practically the same.

The Aqueous Liquid (B).

This liquid, which had a dark brown color, was filtered to remove a small amount of resin. It was then repeatedly extracted with ether, the combined ethereal liquids being washed, dried, and the solvent removed, when about 2 grams of a dark brown, resinous substance were obtained. The latter was redissolved in ether, and the ethereal solution extracted with alkalies, which removed the greater portion of the substance. It gave a violet coloration with ferric chloride and appeared to contain traces of salicylic acid, which had been definitely identified in a corresponding product from the "press-cake," but the amount in the present instance was too small to permit of its isolation.

The aqueous liquid was subsequently treated with a slight excess of basic lead acetate, which produced a voluminous, light brown precipitate. The latter was collected on a filter, well washed, and then suspended in water and decomposed by hydrogen sulphide. After removing the lead sulphide by filtration, a reddish brown liquid was obtained, which gave a dark brown coloration with ferric chloride, indicating the presence of some tannic matter. This liquid was concentrated under diminished pressure, but nothing separated on standing, and, when mixed with purified sawdust, and the dried mixture extracted with various solvents, it yielded nothing crystalline.

The filtrate and washings from the basic lead acetate precipitate possessed a light green color. This was due to the presence of a very small amount of copper, which, by a special test, was found to be contained in the original pumpkin seed.[1] After treatment with hydrogen sulphide for the removal of the excess of lead, and filtering, the liquid was concentrated under diminished pressure to a small bulk. It then had a reddish brown color and contained a quantity of sugar, since it readily yielded *d*-phenylglucosazone, melting at 208°. A portion of the liquid was mixed with purified sawdust and the dried mixture extracted successively with ether, ethyl acetate, and alcohol, but no crystalline substance was removed by these solvents. Another portion of the liquid was treated with dilute sulphuric acid in the manner described in connection with the corresponding liquid from the "press-cake." The products were the same as those yielded by the last-mentioned liquid.

The Resin (C).

The total amount of resinous material obtained from the shells of the pumpkin seed was about 10 grams. It formed a black, brittle mass, and, as already noted, was examined in connection with the larger amount of resin obtained from the "press-cake."

Summary and Conclusions.

In view of the somewhat extended details of the present investigation, a summary of the more important results may here be appended, together with a record of some physiological tests and the deductions therefrom.

---

[1] An account of the wide distribution of copper, in both the vegetable and animal kingdoms, is recorded in the *Am. J. Pharm.*, 77, 274 (1905).

The kernels of the pumpkin seed, separated as completely as possible from the shells, were subjected to strong hydraulic pressure, when they yielded a quantity of fatty oil, together with the so-called "press-cake." These products were then separately examined.

I. *The Fatty Oil.*—The amount of oil obtained from the kernels by expression corresponded to 19.3 per cent. of the weight of the entire seed. The entire seed, when ground and extracted with light petroleum, yielded 34.3 per cent. of fatty oil. The expressed oil, which was optically inactive, possessed the following constants: Specific gravity, 20°/20° = 0.9220; acid value, 3.4; saponification value, 189.4; iodine value, 119.7. The composition of the oil was approximately as follows:

Linoleic acid, as glyceride,	45 per cent.
Oleic acid, as glyceride,	25 "
Palmitic acid Stearic acid } as glycerides,	30 "
	100 "

The oil contains no myristic acid, as has previously been asserted, and of the two solid acids the palmitic acid is in somewhat the larger amount. It contains a very small amount of a phytosterol, $C_{27}H_{46}O$ (m. p. 162–163°), and apparently another substance of this class, having a lower melting point.

II. *The "Press-cake."*—This material was extracted with hot alcohol, and in the resulting product the presence of the following constituents was determined: (1) A quantity of fatty oil, corresponding to 8.7 per cent. of the weight of the entire seed, and agreeing closely in character with that obtained by expression; (2) soluble protein products; (3) a quantity of sugar; (4) a very small amount of salicylic acid; (5) resinous material, amounting to about 0.5 per cent. of the weight of the entire seed. From the resin there were isolated a very small amount of a phytosterol (m. p. 157–159°), apparently identical with that obtained from the expressed oil, and a new *monocarboxylic acid* (m. p. 99°), agreeing in composition with a hydroxycerotic acid, $C_{25}H_{51}O.CO_2H$, which yielded an *ethyl ester* melting at 61°.

III. *The Shells.*—These amounted to 20.8 per cent. of the weight of the entire seed. When extracted with hot alcohol they yielded a fatty oil (amounting to 2.6 per cent. of the weight of the entire seed), which agreed closely in character with that obtained from the kernels by expression. They also contained sugar and a very small amount of resinous material. With the exception of traces of copper, a complete examination of the shells disclosed the presence of no substance which is not contained in the kernel of the seed.

Physiological Tests.

It was finally deemed of interest to ascertain, if possible, whether either the fatty oil or the resin possesses the taenifuge properties which are ascribed to pumpkin seed. For this purpose some preliminary experiments were kindly conducted for us by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, to whom our thanks are due.

The pure expressed oil of pumpkin seed, such as was used for our chemical investigation, was administered in doses of 30 cc., and under the usual conditions of a restricted diet, to two dogs that were known to be afflicted with tapeworm. After an interval of several hours, castor oil was given, but in neither of these cases could any tapeworm be found in the excreta.

One gram of the resin, obtained from the kernel of the seed as above described, was administered to a small dog which had been given no food for 20 hours. Nothing happened during the 6 hours following its administration, and the dog was then given 20 cc. of castor oil. This produced fairly copious, loose evacuations, in which isolated, macerated proglottides were detected, but no considerable length of tapeworm. The resin obtained from the shells or husks of the seed was given to another dog in about the same amount (0 9 gram) as in the preceding experiment, and under similar conditions, but with an equally negative result. While these experiments have thus shown the resin of pumpkin seed to be perfectly innocuous, they have, on the other hand, afforded no indication that it possesses anthelmintic properties.

Through the kindness of several medical practitioners in different parts of the country an opportunity was afforded us of testing the pumpkin seed oil in five cases of tapeworm, four of which occurred in children. The amount of oil administered varied from half a fluidounce to two ounces (15 to 60 cc.), and, although the dose was in some cases repeated, in no instance did it effect the complete removal of the worm. In one of these cases, that of a child of seven years, in which 2 ounces (60 cc.) of the oil had removed a portion of the worm, a trial was subsequently made of the resin from the seed. One gram of this material (representing approximately 200 grams of pumpkin seed) was administered in the early morning, while fasting, and was followed in two hours by a dose of castor oil. No ill effects were observed, and, although the child was purged several times, neither the worm nor any fragment of it appeared.

In conclusion it may be said that the results of the above-described experiments do not enable us to confirm the recorded statements respecting the efficacy of either the fatty oil or the resin of pumpkin seed as a taenifuge. As it is evident that these seeds contain no principle exhibiting marked physiological activity, any value which they may actually possess, when administered in substance for the purpose indicated, would therefore appear to be attributable to a mechanical action. In any case, the remedial value of pumpkin seeds cannot be considered such as to justify their recognition by a national pharmacopoeia.

[CONTRIBUTION FROM THE WELLCOME CHEMICAL RESEARCH LABORATORIES, LONDON.]

CHEMICAL EXAMINATION OF WATERMELON SEED.

BY FREDERICK B. POWER AND ARTHUR H. SALWAY.

Received January 13, 1910

The seeds of the watermelon (*Cucurbita citrullus*, Linné) have been employed to some extent medicinally on account of their diuretic properties, but chiefly as a domestic remedy. So far as known to us, they have never been examined chemically. Lewkowitsch[1] has briefly noted the physical and chemical constants of the fatty oil, and of the mixed fatty acids obtained therefrom, but makes no statement regarding the composition of the oil, and no further information concerning this product appears to be available.

As many of the plants belonging to the family of *Cucurbitaceae* contain in some of their parts substances which possess a considerable degree of physiological activity, it was deemed desirable to submit the seeds of the watermelon to a complete chemical examination. Such an investigation appeared, furthermore, of interest from the point of view of comparing the constituents of these seeds with those of the common pumpkin (*Cucurbita pepo*, Linné), which have recently been completely examined by us.[2]

EXPERIMENTAL.

The material employed was obtained from the United States and consisted of fresh watermelon seeds of good quality.

A portion of the crushed seed was first tested for the presence of an alkaloid by means of Prollius' fluid, but with a negative result.

For the purpose of a complete investigation, 22.5 kilograms of the seed were crushed and the shells separated as completely as possible from the kernels. The shells amounted to 10.95 kilograms, thus corresponding to 48.7 per cent. of the weight of the seed. The ground kernels were then subjected to strong hydraulic pressure, when 1665 grams of fatty oil were obtained, corresponding to 7.4 per cent. of the weight of the entire seed. The so-called "press-cake" remaining after the removal of the oil amounted to 8.88 kilograms. These operations, connected with the expression of the oil, were carefully conducted for us by Messrs. Stafford, Allen & Sons, of London, to whom our thanks are due.

---

[1] "Chemical Technology and Analysis of Oils, Fats and Waxes," 3rd Edit., Vol II, p. 511.

[2] THIS JOURNAL, 32, 346.

A portion of the entire seed, when ground and extracted in a Soxhlet apparatus with light petroleum (b. p. 30–45°), yielded 19.0 per cent. of fatty oil.

I. Examination of the Expressed Oil.

The expressed oil of watermelon seed has a light yellow color and, unlike that from pumpkin seed, is completely devoid of fluorescence. The constants of the oil were determined with the following results:

	Expressed oil.	Oil extracted by petroleum.
Specific gravity 20°/20°	0.9233	0.9219
Acid value	3.9	3.6
Saponification value	191.8	189.9
Iodine value	121.1	121.8

For a complete chemical examination of the oil, 250 grams of it were employed. It was first subjected to distillation with steam, but the distillate contained no volatile oil nor any acid.

Hydrolysis of the Oil.

The oil which had been subjected to distillation with steam, as above described, was separated from the water, the latter then extracted with ether to recover a small amount of suspended oil, and, after adding this to the main portion, the whole was hydrolyzed by heating with an alcoholic solution of 70 grams of potassium hydroxide. The greater portion of the alcohol was then removed, water added, and the alkaline liquid repeatedly extracted with ether. The ethereal liquids were united, washed with a little water, dried with anhydrous sodium sulphate, and the ether removed, when about 0.5 gram of a light yellow oil was obtained, which soon solidified. The solid product, after three crystallizations from a mixture of ethyl acetate and alcohol, separated in pearly leaflets, melting at 163–164°. After drying at 105° it was analyzed:

0.0881 gave 0.2667 CO_2 and 0.0905 H_2O. C = 82.6; H = 11.4.

$C_{20}H_{34}O$ requires C = 82.8; H = 11.7 per cent.

This substance, when dissolved in chloroform with a little acetic anhydride, and a drop of sulphuric acid subsequently added, gave a blue coloration, rapidly changing to green, and finally to brown. It is evidently a phytosterol.

The Fatty Acids.

The alkaline, aqueous solution of potassium salts, which had been extracted with ether as above described, was acidified with sulphuric acid and the mixture distilled with steam. The distillate, however, contained no volatile acid. The fatty acids remaining in the distillation flask were taken up with ether, the ethereal solution being washed, dried, and the solvent removed. For the purpose of determining the constants of the mixed fatty acids, a portion was heated for some time at 100° under diminished pressure, in order to remove the last traces of ether, after which the following results were obtained: M. p. (complete fusion), 35°; d 50°/50° = 0 8894; neutralization value, 198.2; iodine value, 118.2. Optically inactive. A determination of the acetyl value indicated the absence of hydroxy acids.

The mixed fatty acids, which consisted of a liquid and a solid portion, were first partially separated by filtration with the aid of a pump. The solid acids were then fractionally crystallized from alcohol until no further separation could be effected by this means. The least soluble fraction melted at 66–68°, and was considerable in amount. In order to ascertain whether this fraction was homogeneous, it was dissolved in hot alcohol and a measured portion of concentrated, aqueous barium acetate added, drop by drop, with constant stirring. The mixture was then filtered, while still hot, with the aid of a pump, and the precipitate washed with a little hot alcohol. The whole operation was then repeated, and in this manner four successive fractions of barium salt were obtained. The acids liberated from each of these fractions were crystallized once from alcohol, when they had the following melting points: 69–70°, 69–70°, 67–69°, 65–67°. The acid melting at 69–70° separated in glistening, pearly leaflets and was analyzed:

0.1267 gave 0.3522 CO_2 and 0 1448 H_2O. C = 75 8; H = 12.7.

0.5155 neutralized 18.1 cc. 0.1 *N* KOH. Neutralization value = 197.0°.

$C_{18}H_{36}O_2$ requires C = 76.1; H = 12.7 per cent. Neutralization value = 197.5.

It is thus evident that the substance melting at 69–70° was stearic acid, and that no acid of higher carbon content was present.

All the portions of acid obtained in the course of the original fractionation which melted below 66–68° were united and fractionally precipitated with barium acetate in the manner previously described. Six fractions of barium salt were thus obtained, from which the acids were subsequently liberated. The last of these fractions of acid was oily, and to a large extent unsaturated, while the remaining five fractions, after being once crystallized from alcohol, melted at 66–68°, 65–67°, 65–67°, 64–66°, and 57–58°, respectively. Each of these fractions was titrated, with the following results:

Fraction 1 (m. p. 66–68°), 0.2661 neutralized 9.5 cc. 0.1 *N* KOH. N. V. = 200.3.

Fraction 2 (m. p. 65–67°), 0.1356 neutralized 4.8 cc. 0.1 *N* KOH. N. V. = 198.6.

Fraction 3 (m. p. 65–67°), 0.1828 neutralized 6.5 cc. 0.1 *N* KOH. N. V. = 199.5.

Fraction 4 (m. p. 64–66°), 0.0876 neutralized 3.15 cc. 0.1 *N* KOH. N. V. = 201.8.

Fraction 5 (m. p. 57–58°), 0.1707 neutralized 6.35 cc. 0.1 *N* KOH. N. V. = 208.7.

$C_{18}H_{36}O_2$ requires a neutralization value of 197.5.
$C_{16}H_{32}O_2$ requires a neutralization value of 219.1.

From the above results it was evident that fractions 1–4, inclusive, consisted, to a large extent, of stearic acid, while fraction 5 would appear to have contained about equal parts of stearic and palmitic acids.

It may therefore be concluded that the solid fatty acids of watermelon seed oil consist only of palmitic and stearic acids, the latter being present in the larger proportion.

The liquid acids, which had been separated from the solid portion as previously described, constituted the larger proportion of the total fatty acids. In order to separate the small amount of saturated acids still contained in the liquid portion, the whole was converted into a lead salt and this extracted with ether. The portion of lead salt soluble in ether yielded 145 grams of liquid acid, which possessed the following constants: *d* 20°/20° = 0.9027; b. p. 233–240°/20 mm.; neutralization value, 200.1; iodine value, 142.1.

0.1230 gave 0.3433 CO_2 and 0.1293 H_2O. C = 76.1; H = 11.7.
$C_{18}H_{34}O_2$ requires C = 76.6; H = 12.1 per cent.
$C_{18}H_{32}O_2$ requires C = 77.1; H = 11.4 per cent.

The above results indicated that the liquid acid consisted of a mixture of unsaturated acids, and with the endeavor to effect their separation a method was employed which depended on the fractional precipitation of their barium salts. Five fractions of barium salt were thus obtained, each of which was shaken with hydrochloric acid in the presence of ether, the ethereal solution being subsequently washed, dried, and the solvent removed. After heating for a time at 100° under diminished pressure, in order to remove the last traces of ether, the iodine value of the several fractions of acid was determined:

Fraction I 0.1035 of acid absorbed 0.1455 I. Iodine value = 140.6.
Fraction II. 0.1573 of acid absorbed 0.2249 I. Iodine value = 143.0.
Fraction III. 0.1436 of acid absorbed 0.2073 I. Iodine value = 144.4
Fraction IV. 0.0983 of acid absorbed 0.1417 I. Iodine value = 144.2.
Fraction V. 0.0987 of acid absorbed 0.1417 I. Iodine value = 143.6.
$C_{18}H_{34}O_2$ requires an iodine value of 90.1.
$C_{18}H_{32}O_2$ requires an iodine value of 181.4.

The first fraction still contained a small amount of saturated acid, while the iodine values of the remaining four fractions indicated that the latter were practically identical in composition. It was, however, also apparent that a separation of the acids had not been effected by the above-described method.

From the iodine values above noted it could be concluded that the mixture of unsaturated acids consisted of oleic and linoleic acids in approximately equal proportions. In order to confirm this assumption, 30 grams of the mixture were oxidized in alkaline solution with an equal weight of potassium permanganate. The product of oxidation was digested with large quantities of ether, which extracted a substance melting at 126–128° and which, after crystallization from alcohol, separated in small, glistening leaflets melting at 128°.

0.1039 gave 0.2594 CO_2 and 0.1075 H_2O. C = 68.1; H = 11.5.

$C_{18}H_{36}O_4$ requires C = 68.4; H = 11.4 per cent.

This substance was evidently dihydroxystearic acid, and its formation established the presence of oleic acid in the mixture of liquid acids.

The oxidation product, after extraction with ether, was heated with large quantities of water, and the liquid filtered while hot. These deposited a pure white, crystalline substance, melting at 154–155°, which, after crystallization from alcohol, separated in small, thin needles, melting at the same temperature.

0.1138 gave 0.2574 CO_2 and 0.1068 H_2O. C = 61.7; H = 10.4.

$C_{18}H_{36}O_6$ requires C = 62.1; H = 10.3 per cent.

This substance was thus identified as tetrahydroxystearic acid (sativic acid), and its formation established the presence of linoleic acid in the mixture of liquid acids. As no hexahydroxystearic acid could be isolated from the product of oxidation, it may be concluded that linolenic acid is not a constituent of the oil.

II. Examination of the Press-cake.

The so-called "press-cake" resulting from the expression of 22.5 kilograms of watermelon seeds, deprived as completely as possible of the shells, amounted, as previously noted, to 8.88 kilograms. This was completely extracted with hot alcohol, when, after the removal of the greater portion of the alcohol, a thin, dark brown, oily extract was obtained, amounting to 1644 grams. It evidently contained a considerable quantity of fatty oil which had escaped expression from the seed, and which was removed by treating the extract with light petroleum (b. p. 30–45°). The amount of fatty oil obtained in this way was 1340 grams, thus corresponding to 81.5 per cent. of the total alcoholic extract. Its constants were as follows: *d* 20°/20° = 0.9328; saponification value, 191.4; iodine value, 112.7.

The fatty oil obtained from the press-cake, as above described, would naturally be expected to be similar in composition to that obtained from the seed by expression, and its examination proved this to be the case. It was found to contain a very small amount of a phytosterol, melting at 160°, and the mixed fatty acids obtained on hydrolysis possessed the following constants: m. p., 34°; *d* 50°/50° = 0.8916; neutralization value, 197.6; iodine value, 129.5. These acids, like those obtained from the expressed oil, consisted of a mixture of palmitic, stearic, oleic and linolic acids.

The portion of the alcoholic extract which remained undissolved by treatment with light petroleum was subjected to distillation with steam, but no volatile product was obtained. The contents of the distillation flask then consisted of a dark colored aqueous liquid (*A*) and a quantity of a black resin (*B*), which were separated by filtration and the resin well washed with water.

The Aqueous Liquid (A).

The aqueous liquid was repeatedly extracted with ether, the ethereal liquids being washed, dried, and the solvent removed. About 0 5 gram of a viscid, brown oil was thus obtained, which deposited nothing in the cold, and which, in alcoholic solution, gave with ferric chloride a green coloration. The oily product was digested with a large volume of light petroleum, but no crystalline substance could be isolated from it. It was thus ascertained that the seed of the watermelon, unlike those of the pumpkin, do not contain salicylic acid.

Treatment with Basic Lead Acetate.

The aqueous liquid, which had been extracted with ether as above described, was subsequently treated with basic lead acetate, which yielded a yellowish brown precipitate. The latter was collected on a filter, thoroughly washed, and then suspended in water and decomposed by hydrogen sulphide. On filtering the mixture and concentrating the filtrate under diminished pressure, a reddish brown liquid was obtained, which gave a bluish black coloration with ferric chloride, thus indicating the presence of tannin. As the liquid deposited only a little amorphous material on standing, it was finally mixed with purified sawdust and the dried mixture extracted successively in a Soxhlet apparatus with ether, ethyl acetate and alcohol. These solvents, however, did not effect the separation of any crystalline substance.

The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, filtered, and this filtrate concentrated under diminished pressure. A reddish brown, sirupy liquid was thus obtained, which contained a large amount of sugar, since it readily yielded *d*-phenylglucosazone, melting at 210°. The liquid gave a precipitate with potassium-mercuric iodide, and on heating with alkalies evolved ammonia, but these reactions were evidently due to protein products and not to the presence of an alkaloid, since the entire seed, when tested for substances of this class by means of Prollius' fluid, gave a perfectly negative result.

A portion of the aqueous liquid which had been purified by treatment with basic lead acetate, as above described, was heated for some time in a reflux apparatus with such an amount of sulphuric acid that the latter represented 5 per cent. by weight of the mixture. During the operation a quantity of resinous material separated, which was quite insoluble in the usual organic solvents. On subsequently passing steam through the liquid a slightly acid distillate was obtained, in which the presence of formic and acetic acids was determined. The acid, aqueous liquid which remained in the distillation flask was repeatedly extracted with ether, which, however, removed only traces of brown, amorphous material. No evidence was thus obtained of the presence in the aqueous liquid of any definite substance of a glucosidic nature.

The Resin (B).

The resin from the "press-cake" amounted to 70 grams. The greater portion of this material (68 grams) was digested with hot alcohol, then mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 30–45°) extracted	27.0 grams	=	39.7 per cent.
Ether	"	3.8 "	=	5.6 "
Chloroform	"	3.0 "	=	4.4 "
Ethyl acetate	"	2.2 "	=	3.2 "
Alcohol	"	15.5 "	=	22.8 "
Total,		51.5 "	=	75.7 "

By this process of extraction a considerable portion of the resin had evidently been rendered insoluble.

Petroleum Extract of the Resin.

This was a dark-colored, viscid product. It was heated in a reflux apparatus with an excess of an alcoholic solution of potassium hydroxide, the greater portion of the alcohol then removed, water added, and the alkaline mixture extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when a very small quantity (0.2 gram) of a light yellow solid was obtained. This was crystallized from a mixture of ethyl acetate and alcohol, when it melted at 158–159°. It was a phytosterol and apparently identical with that previously isolated from the expressed oil of the seed.

The alkaline, aqueous liquid, from which the above-mentioned phytosterol had been separated, was acidified with sulphuric acid and extracted with ether. During the extraction a small quantity of resinous matter separated, which was removed by filtration. This was dried on a porous tile, and then dissolved in pyridine, when it yielded a crystalline substance which, after a few crystallizations from the same solvent, separated in colorless, prismatic needles, melting and decomposing at about 260°. It was found to be identical with a new substance, $C_{24}H_{40}O_4$, which was subsequently isolated from the ether extract of the resin, as described below.

The ethereal liquid, as above obtained, was washed, dried, and the solvent removed, when it yielded a mixture of fatty acids. This was distilled under diminished pressure, when it passed over between 230 and 245°/25 mm., leaving only a small amount of resin. The distilled product, on cooling, became partially solid. The solid portion was therefore separated by filtration, with the aid of the pump, and crystallized from alcohol, when it was obtained in glistening plates, melting at 60–62°.

0.3561 neutralized 32.2 cc. 0.1 *N* KOH. Neutralization value = 208.0.
$C_{18}H_{36}O_2$ requires a neutralization value of 197.5.
$C_{16}H_{32}O_2$ requires a neutralization value of 219.1.

The product evidently consisted of a mixture of palmitic and stearic acids in about equal proportions.

The liquid acids which had been separated from the solid portion by filtration were for the most part unsaturated, since they readily absorbed bromine, and the presence of oleic acid was also indicated by the behavior towards nitric acid.

The fatty acids contained in the petroleum extract of the resin were therefore the same as those obtained from the expressed oil of watermelon seeds.

Ether Extract of the Resin.

Isolation of a New Alcohol, Cucurbitol, $C_{24}H_{40}O_4$.—The ether extract of the resin was a dark brown, soft mass, and amounted to only 3.8 grams. It was digested with cold alcohol, which removed the coloring matter, while the greater portion of the material remained as a yellowish brown powder. This was collected on a filter and washed with a little cold alcohol, after which it was dissolved in warm pyridine. From this solution a substance separated in the form of radiating clusters of colorless needles, which, when slowly heated, melted and decomposed at 260°. The substance, after drying at 110°, was analyzed:

0.0626 gave 0.1680 CO_2 and 0.0587 H_2O. C = 73.2; H = 10.4
$C_{24}H_{40}O_4$ requires C = 73.5; H = 10.2 per cent.

The substance is thus seen to agree in composition with the formula $C_{24}H_{40}O_4$. When dissolved in chloroform with a little acetic anhydride, and a drop of concentrated sulphuric acid subsequently added, a blue coloration is produced, which slowly becomes greenish, and finally dull brown. When heated with acetic anhydride it yielded an acetyl derivative which crystallized in radiating clusters of fine needles, melting at 150°. The acetyl derivative is very soluble in ethyl acetate and moderately so in alcohol, but the amount available was not sufficient for analysis.

No substance of the formula $C_{24}H_{40}O_4$, possessing properties similar to those above described, has hitherto been recorded. With consideration, therefore, of the source and alcoholic nature of the new compound, it is proposed to designate it *cucurbitol.*

It is of interest to note, in this connection, that two substances of alcoholic nature, which appear to be closely related to cucurbitol, have recently been isolated in these laboratories. One of these was obtained from the resin of *Grindelia camporum*, Greene, and agrees in composition with the formula $C_{23}H_{38}O_4$. It melts at 256–257°, and yields an acetyl derivative melting at 161°.[1] This compound, which was not previously named, may now be conveniently designated *grindelol.* The other substance was obtained from jalap resin and possesses the formula $C_{21}H_{34}O_4$.[2] The latter compound, designated *ipurganol,* melts at 222–225° and yields an acetyl derivative melting at 166–167°. The three substances, cucurbitol, grindelol, and ipurganol, show slight differences in their color reactions when subjected to the above-mentioned test in chloroform solution with acetic anhydride and concentrated sulphuric acid. Thus ipurganol gives at first a purplish pink coloration, changing to blue, then becoming bright green, and finally brown, while grindelol gives at first a blue color, which changes to a duller green than the preceding, and finally becomes brown, and in the case of cucurbitol the intermediate greenish tint is still less pronounced. In view of the composition and character of these three new compounds, it is evident that they are members of a homologous series, which is represented by the general formula $C_nH_{2n-8}O_4$.

Chloroform, Ethyl Acetate and Alcohol Extracts of the Resin.

The chloroform and ethyl acetate extracts were both very small in amount (3.0 and 2.2 grams respectively), and, like the alcohol extract of the resin, formed brittle, black solids. They were all carefully examined, but nothing definite could be isolated from them.

III. Examination of the Shells.

The shells from 22.5 kilograms of watermelon seeds amounted to 10.95 kilograms, thus corresponding to 48.7 per cent. of the weight of the seed. This material was ground and extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, a dark-colored, oily product was obtained, which contained some resin in suspension. The entire amount of extract (907 grams) was first mixed with a large volume of light petroleum, in order to effect the separation of the fatty oil (*A*). The portion of extract remaining undissolved by the petroleum may be designated as (*B*).

The Fatty Oil (A).

The petroleum solution of the fatty oil was filtered, dried with anhydrous sodium sulphate, and the solvent removed. A dark green, opaque oil was thus obtained, which amounted to 750 grams, or 82.7 per cent. of the total alcoholic extract. It possessed the following constants: d 20°/20° = 0.9351; saponification value, 191.3; iodine value, 114.6.

---

[1] Compare *Proc. Am. Pharm. Assoc.*, 55, 342 (1907).

[2] THIS JOURNAL, 32, 89.

For the examination of the fatty oil 150 grams of it were employed. This was brought into a flask with a little water and steam passed through the mixture, but the distillate contained only traces of volatile acid.

Hydrolysis of the Oil.

The fatty oil remaining in the distillation flask after the above-mentioned treatment with steam was separated from the water and hydrolyzed by heating with an alcoholic solution of 40 grams of potassium hydroxide. The greater portion of the alcohol was then removed, water added, and the alkaline solution extracted repeatedly with ether. The ethereal liquids were united, washed with water, dried with anhydrous sodium sulphate, and the solvent removed. About 0.5 gram of a solid substance was thus obtained, which crystallized readily from a mixture of ethyl acetate and alcohol. It first melted at 140°, and after a second crystallization separated in pearly leaflets, melting at 141–142°. After drying at 105° it was analyzed:

0.0970 gave 0.2930 CO_2 and 0.1012 H_2O. C = 82.4; H = 11 6.
$C_{20}H_{34}O$ requires C = 82 8; H = 11.7 per cent.

This substance is thus seen to be a phytosterol, and its identity was further confirmed by the characteristic color reactions.

The Fatty Acids.

The alkaline, aqueous solution of potassium salts, which had been extracted with ether as above described, was acidified with sulphuric acid and again extracted with ether, the ethereal solution being washed, dried, and the solvent removed. A dark brown, semi-solid mass of fatty acids was thus obtained, which possessed the following constants: M. p., 32°; d 50°/50° = 0.8968; neutralization value, 200 2; iodine value, 115.8.

The acid, aqueous liquid which had been extracted with ether was distilled with steam, but the distillate contained only traces of volatile acid.

The mixed fatty acids were first separated into a solid and a liquid portion by filtration with the aid of a pump. The solid portion was then fractionally crystallized from alcohol, when the least soluble fraction, on further crystallization, melted successively at 63–66°, 66–68°, 68–69°, and finally at 71°. It was thus evident that some acid of higher carbon content than stearic acid was present, and the substance melting at 71° was analyzed:

0.1060 gave 0.2968 CO_2 and 0.1201 H_2O. C = 76.4; H = 12.6.
$C_{18}H_{36}O_2$ requires C = 76.1; H = 12.7 per cent.
$C_{20}H_{40}O_2$ requires C = 76.9; H = 12.8 per cent.

This substance thus appeared to consist of a mixture of stearic and arachidic acids, and the separation of the latter in a pure state was subsequently accomplished by the fractional distillation of the solid portion of mixed fatty acids. On distilling the solid acids under diminished pressure, they began to boil at 230°/18 mm., but nearly the entire amount passed over between 233 and 240°/18 mm., while a small final fraction was collected at 240–250°/18 mm. The last-mentioned fraction readily solidified on cooling, and was then crystallized twice from ethyl acetate, from which it separated in rosettes of glistening leaflets, melting at 76–78°.

0.0935 gave 0.2633 CO_2 and 0.1077 H_2O. C = 76.8; H = 12 8.
$C_{20}H_{40}O_2$ requires C = 76 9; H = 12.8 per cent

The identity of this substance as arachidic acid was thus established.

The fraction of acid distilling at 230–233°/18 mm. melted at 59–60°, while that collected between 233 and 240°/18 mm. melted at 62–64°. Both of these fractions consisted of mixtures of palmitic and stearic acids.

The liquid portion of the mixed fatty acids was highly unsaturated, and, like the corresponding product from the expressed oil of the seed, evidently consisted of a mixture of oleic and linoleic acids.

Portion of Alcoholic Extract Insoluble in Petroleum (B).

This portion of the original extract of the shells formed a black, resinous mass, amounting to 150 grams. It was mixed with water and distilled with steam, but the distillate contained only traces of volatile acid. The contents of the distillation flask then consisted of a light yellow, aqueous liquid and a quantity of a black resin. These were separated by filtration and the resin well washed with water.

The Aqueous Liquids.

The above-mentioned, yellow, aqueous liquid was repeatedly extracted with ether, which removed about 1 gram of a brownish yellow oil. On digesting this product with water, the resulting liquid gave a greenish coloration with ferric chloride. The oily product was practically insoluble in water and only partially soluble in sodium carbonate, but dissolved completely in a solution of sodium hydroxide, and was therefore phenolic in character. It was distilled under diminished pressure, whereby some resinous material was removed, and then benzoylated. A crystalline solid melting at 205–210° was thus obtained, but the amount was much too small for further examination.

The aqueous liquid was subsequently treated with a slight excess of basic lead acetate, which yielded a relatively small amount of a yellowish precipitate. This was collected, washed, suspended in water, and decomposed by hydrogen sulphide. On filtering the mixture a liquid was obtained which gave a bluish black coloration with ferric chloride, indicating the presence of tannin, but no definite compound could be isolated from it.

The filtrate from the basic lead acetate precipitate possessed a light green color. This was due to the presence of a very small amount of copper, which, by a special test, was subsequently found to be contained in the original watermelon seed.[1] After treatment with hydrogen sulphide for the removal of the excess of lead, and filtering, the liquid was concentrated under diminished pressure. A light yellow sirup was thus obtained, which deposited nothing crystalline on standing. It contained a quantity of sugar, since it readily reduced Fehling's solution, and yielded *d*-phenylglucosazone, melting at 212–213°.

The aqueous liquid, when heated with alkalies, developed ammonia, which was evidently due to the presence of soluble protein compounds, but it was observed that a peculiar basic odor was also produced. In order to ascertain whether by this treatment any volatile base other than ammonia was formed, a portion of the liquid was heated with baryta in a current of steam, the volatile product being collected in hydrochloric acid. The salt thus obtained, which was small in amount, was converted into the platinum compound, and the latter, after drying in a vacuum over sulphuric acid, was analyzed:

0.0785 of the salt gave, on ignition, 0.0340 Pt. Pt = 43 3.
$(NH_4)_2PtCl_6$ requires Pt = 43.9 per cent.

This salt, therefore, was practically pure ammonium chloroplatinate.

Another portion of the aqueous liquid was heated in a reflux apparatus with such an amount of sulphuric acid that the latter represented 5 per cent. of the weight of the mixture. On distilling the product with steam, only small quantities of formic and acetic acid were obtained, and the contents of the distillation flask, when subsequently extracted with ether, likewise yielded nothing which would indicate the presence of a glucoside in the original aqueous liquid.

A portion of the aqueous liquid was finally mixed with purified sawdust and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with ether, ethyl acetate and alcohol, but no definite substance could be isolated by means of these solvents.

The Resin.

The black, resinous material contained in the portion of alcoholic extract which was insoluble in petroleum, and which had been separated from the aqueous liquid, as above described, amounted to 68 grams. The greater part (66 grams) of this material was digested with alcohol, then mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with various solvents. The results were as follows:

---

[1] An account of the wide distribution of copper, in both the vegetable and animal kingdoms, is recorded in the *Am. J. Pharm.*, 77, 274 (1905).

Petroleum (b. p. 30–45°)	extracted	25.6 grams	= 38.8 per cent.
Ether	"	3.2 "	= 4.8 "
Chloroform	"	9.2 "	= 13.9 "
Ethyl acetate	"	3.4 "	= 5.2 "
Alcohol	"	7.4 "	= 11.2 "
Total,		48.8 "	= 73.9 "

Petroleum Extract of the Resin.

This extract was a dark, viscid liquid. On the addition of ether a small quantity of a gelatinous substance separated, which was removed by filtration. This substance was very sparingly soluble in alcohol, but readily soluble in hot acetic acid, and also in pyridine, from both of which solvents it was again deposited in a gelatinous form.

The portion of the extract which was soluble in ether was heated with an alcoholic solution of potassium hydroxide. After removing the alcohol, water was added and the alkaline liquid extracted with ether. The ethereal liquid, after the removal of the solvent, yielded about 0.5 gram of a light yellow solid, which, when crystallized from a mixture of ethyl acetate and alcohol, separated in glistening leaflets, melting at 138–140°. The melting point and color reactions of this substance indicated that it was identical with the phytosterol, $C_{20}H_{34}O$ (m. p. 141–142°), obtained from the fatty oil of the shells of watermelon seeds.

The alkaline solution of potassium salts, after extraction with ether, was acidified with sulphuric acid and again treated with ether, the ethereal liquid being washed, dried and the solvent removed. The fatty acids thus obtained were distilled under diminished pressure, when the greater portion passed over between 235 and 240°/20 mm., a small fraction having also been collected at 240–260°/20 mm. The fraction 235–240°/20 mm. became partially solid on cooling. The solid portion was therefore removed and crystallized from alcohol, when, after the first crystallization, it melted at 55–58°.

0.3334 neutralized 12.05 cc. 0.1 *N* KOH. Neutralization value = 202.8.

$C_{18}H_{36}O_2$ requires a neutralization value of 197.5.

$C_{16}H_{32}O_2$ requires a neutralization value of 219.1.

It was thus evident that the above portion of solid acid consisted of a mixture of palmitic and stearic acids, the former predominating.

The liquid portion of fatty acids from the fraction 235–240°/20 mm., when tested with nitric acid, was found to contain some oleic acid.

0.2331 absorbed 0.3301 iodine. Iodine value = 141.6.

These liquid fatty acids, therefore, like those contained in the expressed oil of watermelon seeds, evidently consisted of a mixture of oleic and linoleic acids.

The small fraction of acid collected at 240–260°/20 mm. solidified in the receiver. After two crystallizations from alcohol it separated in glistening leaflets, melting at 76–77°. This substance was identified as arachidic acid.

Ether Extract of the Resin.

This extract was a dark brown solid and very small in amount (3.2 grams). It was digested with cold alcohol, which removed the coloring matter, leaving a light brown, amorphous powder. On treating the latter with pyridine a few needle-shaped crystals were deposited, together with some amorphous, brown material. The crystalline substance, which was mechanically separated, melted and decomposed at 260°, and yielded an acetyl derivative melting at 150°. It gave the characteristic color reaction of *cucurbitol*, $C_{24}H_{40}O_4$, and was identical in every respect with the latter compound, as isolated from the "presscake" of watermelon seeds.

Chloroform, Ethyl Acetate and Alcohol Extracts of the Resin.

These were all dark colored, brittle solids, from which no crystalline substance could be obtained.

Summary.

The results of the present investigation of watermelon seeds may be summarized as follows:

The seeds contain no alkaloid, and no evidence was obtained of the presence of a glucoside.

1. *The Fatty Oil.*—The amount of oil obtained from the kernels by expression corresponded to 7.4 per cent. of the weight of the entire seed. The entire seed, when ground and extracted with light petroleum, yielded 19.0 per cent. of fatty oil. The amount of the latter is, therefore, very much less than was obtained by us from pumpkin seed.[1] The expressed oil, which was optically inactive, possessed the following constants: Specific gravity, 20°/20° = 0.9233; acid value, 3.9; saponification value, 191.8; iodine value, 121.1. The composition of the oil was approximately as follows:

Linoleic acid, as glycerides,	45	per cent.
Oleic acid, as glyceride,	25	"
Palmitic acid Stearic acid } as glycerides,	30	"
	100	"

Of the two solid acids, the stearic acid is in predominating amount. The oil contains, furthermore, a very small amount of a phytosterol, $C_{20}H_{34}O$ (m. p. 163–164°). It is thus seen that this oil agrees very closely in composition with the expressed oil of pumpkin seed examined by us.[1]

---

[1] THIS JOURNAL, 32, 351.

II. *The "Press-cake."*—This material was extracted with hot alcohol, and in the resulting extract the presence of the following constituents was determined: (1) A quantity of fatty oil, corresponding to about 6 per cent. of the weight of the entire seed, and agreeing closely in character with that obtained by expression; (2) soluble protein products; (3) a quantity of sugar; (4) resinous material, amounting to about 0.3 per cent. of the weight of the entire seed. From the resin there were isolated a very small amount of a phytosterol (m. p. 158–159°), and a new alcohol, designated *cucurbitol*, $C_{24}H_{40}O_4$ (m. p. 260°), which yields an acetyl derivative melting at 150°. Cucurbitol appears to be closely related to two other crystalline alcohols recently isolated in these laboratories, namely, *grindelol*, $C_{23}H_{38}O_4$ (m. p. 256–257°), from *Grindelia camporum*, which yields an acetyl derivative melting at 161°, and *ipurganol*, $C_{21}H_{31}O_4$ (m. p. 222–225°), from jalap resin, which yields an acetyl derivative melting at 166–167°. These three alcohols are evidently members of a homologous series, which is represented by the general formula $C_nH_{2n-8}O_4$.

III. *The Shells.*—These amounted to 48.7 per cent. of the weight of the entire seed. They contained a quantity of fatty oil, which was similar in character to that obtained from the kernels by expression, but, in addition to the fatty acids obtained from the latter, a small amount of arachidic acid was isolated. The resinous material contained in the shells corresponded to about 0.3 per cent. of the weight of the entire seed, and from it, besides a mixture of fatty acids, very small quantities of a phytosterol (m. p. 138–140°) and *cucurbitol*, $C_{24}H_{40}O_4$, were separated. It was observed that these shells, like those of the pumpkin seed, contain traces of copper.

In order to ascertain whether the resin obtained from watermelon seed possesses any physiological activity, some tests were kindly conducted for us by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories. The resin, both from the kernels and the shells of the seed, was administered to a dog in amounts of one gram each, but no obvious effect was produced, and it may therefore be considered quite innocuous.

THE CONSTITUTION OF RETENE AND ITS DERIVATIVES.

By John E. Bucher.

Received January 13, 1910.

In the early part of the work in this laboratory on the condensation of aromatic propiolic acids to derivatives of 1-phenyl-2,3-naphthalenedicarboxylic acid,[1] much difficulty was experienced in determining the structure of the latter compounds. They could be transformed into carboxylic acids of diphenyl, diphenyleneketone and fluorene. A comparatively small number of such acids are described in the literature and in some cases the structure given is evidently uncertain or else incorrect. They did not aid materially in determining the structure of the naphthalene products. Later in the work, very efficient methods for determining the nature of the products under investigation were found. These methods were found equally applicable for determining the constitution of the derivatives of diphenyl, diphenyleneketone and fluorene, as well as the substances of which these are oxidation products.

---

[1] This Journal, 32, 358.

It was found, for instance, that the constitution of retene could be shown very easily by applying three of these methods.[2] The first method used was that of oxidizing substances in pyridine solution with potassium permanganate. The second depends on the fact that diphenyleneketone-carboxylic acids are very easily oxidized to benzene polycarboxylic acids by alkaline potassium permanganate, if the oxidation is finished by means of fuming nitric acid, aided by the catalytic action of manganese nitrate. The third depends on the fact that when diphenyleneketone-carboxylic acids are heated with potassium hydroxide, the ring breaks in such a way as to have the carboxyl groups as far apart as possible.

Retene, $C_{18}H_{18}$, was examined early in the work, hoping that it would be of service in connection with the above investigation. It is designated as 8-methyl 5-isopropylphenanthrene (I) in such standard works as those of Beilstein and V. von Richter. The numerous derivatives are also assigned corresponding structural formulas, in nearly all cases, without even a question mark, as is shown in the example of reteneketone in Richter's "Lexikon der Kohlenstoffverbindungen."

On looking up the original work of Bamberger and Hooker,[3] it was seen that there was no justification for this distribution of the two substituting groups. They showed, in their very careful research, that retene is a methylisopropylphenanthrene but they were not able to determine the position of the two groups. They state positively that they did not prove that the groups are in the para (5,8-) position or even that they are both united to the same benzene nucleus. They thought one group to be in the ortho (8-) position, however. The diphenyleneketone-dicarboxylic acid (V) obtained from retene does not yield an anhydride easily. When this acid is heated with potassium hydroxide it yields a diphenyltricarboxylic acid. On page 114, they state that this acid yields a fluorescein, thus showing that the groups are in the ortho position. On

[1] This Journal, 30, 1244 (1908).

[2] *Ibid.*, 32, 219 (1910).

[3] *Ann.*, 229, 114 (1885).

page 161, they describe the same acid as not changing in any way *even at* 270°. They, as well as nearly all of those who used this argument, evidently overlooked this contradiction. Even if an acid (VI) not splitting out water were formed quantitatively, it would still be possible that the groups were in the ortho position originally. Failure to consider the possibility of isomeric acids has led to uncertainty in other cases in assigning structural formulas to derivatives of diphenyl, diphenyleneketone and other substances of this kind. Since there are *twenty-eight* isomers possible, considering only two rings, in the case of retene, it is evident that the formula given in the literature has no value. The idea of getting substances of known structure from this hydrocarbon was therefore abandoned for a time.

A little later it was pointed out by Fortner[1] that the formula of retene must be incorrect. He synthesized a 2-diphenyleneketonecarboxylic acid which was found to be identical with one obtained from retene by Bamberger and Hooker. This showed that one of the groups in retene must be in position 2- but he was not able to determine which one.

Schultze[2] in working on resin-oils, showed that they contain hydrogenated retenes. He showed that these could be transformed into retene and also that they could be oxidized to *1,2,4-benzenetricarboxylic acid.* This observation proves that the two groups cannot be on the same benzene ring. The same observation had also been made by earlier observers, only one might question whether their compounds were pure enough to be used for work on the constitution of retene.

Lux[3] also investigated the constitution of retene. By fusion of reteneketone with potassium hydroxide, he obtained two methylisopropyldiphenylcarboxylic acids. One of these acids did not esterify easily and he concluded that it must contain two substituting groups in the ortho positions to the carboxyl group. This was used to show that in retene one group must be in the meta position (8-) compared with the diphenyl. He was not able to determine whether this group was methyl or isopropyl. As a result of the work of Fortner, Schultze, Lux and others, it follows that the formula (I) of Bamberger and Hooker cannot be correct but that retene probably has a structure represented either by formula II or III.

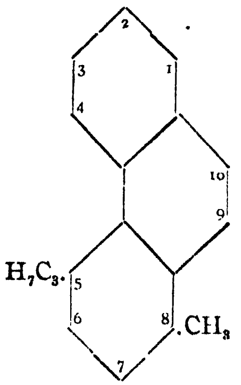
In addition to these, Easterfield and Bagley have advocated the formula with the methyl group in position 8- and the isopropyl group in position 6-. It will be shown in the latter part of this paper in discussing the structure of abietic acid (VII), that some of the evidence upon which they base this formula is really the strongest evidence which can be cited against it.

---

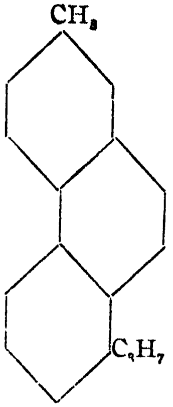
[1] *Monatsh. Chem.*, 29, 763 (1904).

[2] *Ann.*, 359, 132 (1908).

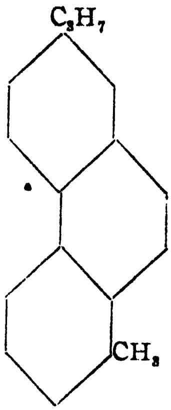
[3] *Monatsh. Chem.*, 35, 452 (1908).



I.



II.

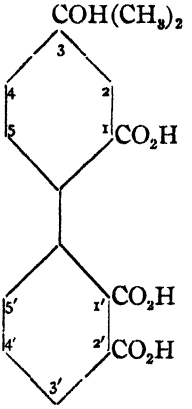


III.

In our study of the oxidation of organic substances in pyridine solution in this laboratory, we obtained compounds which give a perfectly satisfactory solution of this problem—the properties of the oxyisopropyldiphenyltricarboxylic acid obtained in the following manner showing the position of the methyl group in retene.

Ten grams of retenequinone are dissolved in 50 cc. of pyridine and 25 cc. of water in a three-liter flask, provided with a reflux condenser. The flask is heated on the water bath and in the course of half an hour 60 grams of finely powdered potassium permanganate are added in about six portions. The flask is shaken vigorously during the process and more water is added, as needed, to keep the contents in a pasty condition. The total quantity of water present at the end of the experiment should be about 100 cc. The heating and shaking were continued until the permanganate was all reduced. The whole operation required about one hour. The pyridine was then recovered by distilling it with a current of steam until the odor had disappeared. The oxides of manganese were then removed by filtration and 1.1 grams of unchanged retenequinone recovered from them. The warm filtrate was then oxidized with 10 grams of potassium permanganate to complete the process. When the color had disappeared, the solution was filtered, made nearly neutral with sulphuric acid and concentrated to a small bulk to remove the potassium sulphate. It was then acidified and extracted with ether. On distilling off the ether, a mixture of acids was left in the form of a sirup. After the addition of a small quantity of water, the solution was boiled *in vacuo* until the odor of ether disappeared. It was then allowed to evaporate spontaneously nearly to dryness. On taking up the acids with a little warm water, one sparingly soluble acid could be separated from the other very soluble acids. After crystallizing from water, 2.2 grams were obtained.

The acid titrated for a tribasic acid with a molecular weight of 345. The theory for an hydroxyisopropyldiphenyltricarboxylic acid (IV) is 344.

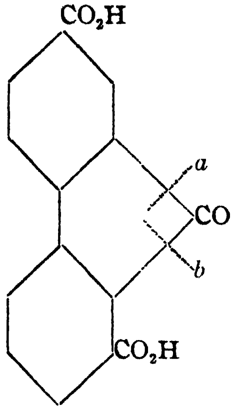


IV.

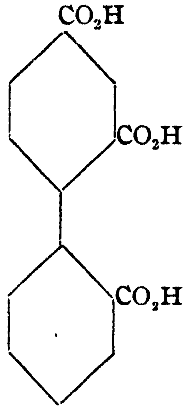
The acid loses water easily upon heating, leaving a residue which is still soluble in sodium carbonate. This shows the acid to be tribasic. The formation from retenequinone shows the position of groups 1- and 1′-. The formation of water on heating shows another carboxyl group in an adjacent ortho position (2′-). As the isopropyl residue remains in the compound, it is certain that group 2′- must have come from the methyl group. It follows from this that the methyl group must be in position 8- in retene. This excludes formula II and shows that formula III for an 8-methyl-2-isopropylphenanthrene must represent the structure of retene.

This experiment also yields other important evidence. On further oxidation the oxyisopropyl acid (IV) yields the corresponding tetrabasic acid which is easily soluble in water and gives diphenyl for the hydrocarbon. This tetrabasic acid, on heating, gave off water but the residue dissolved in sodium carbonate with effervescence. The acid, therefore, does not contain a carboxyl group in position 2 (formula IV). Also, a small quantity of *1,2,3-benzenetricarboxylic acid* was obtained—proving that in retene the groups must be united to different rings. These products alone are sufficient to determine the general structure of retene—the only point left open in formula III being whether the isopropyl group is in position 2, 3 or 4. There can be no doubt that the other acids which are formed in this one oxidation experiment will enable us to tell which of these three possibilities is the true one.

However, it was thought easier to oxidize the diphenyleneketone dicarboxylic acid (V) which Bamberger and Hooker obtained from retene by oxidation.



V.



VI.

Bamberger and Hooker state that this acid is oxidized to oxalic acid by potassium permanganate. This view is misleading, however, as comparatively small quantities of oxalic acid are formed. It has been shown that acids of this type are oxidized very readily to the corresponding benzenepolycarboxylic acids.[1] One would expect this particular acid to break up at *a* and *b*, thus yielding *two* isomeric benzenetricarboxylic acids.

Accordingly, one gram of this yellow ketonic acid was oxidized with potassium permanganate in the usual way. After filtering off the oxides of manganese, the solution was concentrated, acidified and extracted with ether. The sirupy solution of acids was heated in an evaporating dish over the water bath to expel the last traces of ether. Fuming nitric acid and a crystal of manganese nitrate were then added. Brisk effervescence, due to the oxidation of oxalic acid and probably some —$CO.CO_2H$ groups, took place at once and a white solid acid separated. The solution was evaporated to dryness and the acid washed with fuming nitric acid and then recrystallized from water. The acid separated in clear massive crystals, which are characteristic of 1,2,3-benzenetricarboxylic acid. It titrated for a molecular weight of 246 and lost 14.45 per cent. of water at 100°. Theory for 1,2,3-$C_6H_3(CO_2H)_3.2H_2O$; $M = 246$, $H_2O = 14.63$ per cent. The water of crystallization serves to distinguish it from the isomeric 1,2,4-benzenetricarboxylic acid which occurs in the filtrate and separates at ordinary temperatures without water of crystallization. The crystals of the latter acid are also quite different so there was no trouble in recognizing it. Both gave excellent yields of benzene for the hydrocarbon.

The isolation of both these acids limits the structure of retene, at once, to one group in position 8- and the other group in either position 2- or

---

[1] THIS JOURNAL, 32, 220 (1910).

3-. It also excludes Bamberger and Hooker's formula, which would necessitate the formation of 1,2,3,4-benzenetetracarboxylic acid and phthalic acid. Taken in connection with the above oxidation in pyridine solution the only question left open is whether the isopropyl group in formula III is in position 2- or 3-.

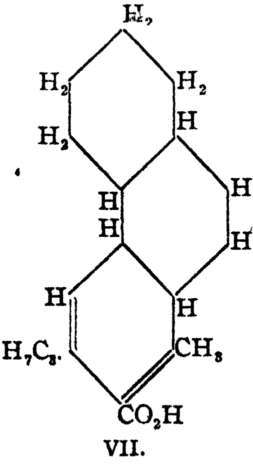
The oxidation of the diphenyleneketonedicarboxylic acid (V) was also effected in the following way. Heating this acid with potassium hydroxide should lead to the formation of the acid represented by formula VI, the ring breaking at *b*. The acid obtained in this way did not split out water upon heating, confirming the view that the statement made by Bamberger and Hooker on page 161 in their article is correct and that the structure they suggest on page 114 is incorrect. This 1,3,2'-diphenyltricarboxylic acid was then dissolved in 5 parts of fuming nitric acid, the solution being boiled ten minutes in the water bath. It was then evaporated to dryness in a casserole, taken up in hot water and reduced with sodium amalgam. The oxidation was then carried on exactly as in the preceding experiment, except that concentrated nitric acid was used instead of fuming acid in the final treatment with nitric acid and manganese nitrate. This avoids the danger of getting nitro acids. As expected, this experiment gave a small quantity of meta-phthalic acid and a large quantity of 1,2,4-benzenetricarboxylic acid. The latter acid contained no water of crystallization, titrated for a molecular weight of 212 and gave a good yield of benzene for the hydrocarbon. These results are in thorough accord with those obtained by the direct oxidation of the yellow ketonic acid (V).

On oxidizing reteneketone, Bamberger and Hooker obtained a mixture of the diphenyleneketonedicarboxylic acid (V) and the corresponding hydroxyisopropyldiphenyleneketonemonocarboxylic acid. We have shown that this mixture can be used in the above experiments instead of the pure dibasic acid—thus avoiding a very tedious process of purification. As there is no danger of ambiguous results, this mixture was also used in the following experiment: It was heated with potassium hydroxide at 218° to break up the ketone ring and form the corresponding acid derivatives of diphenyl. The resulting acids were reduced with hydriodic acid at 200° in the hope of reducing the hydroxyisopropyl group to the isopropyl group. The hydrocarbon was then prepared in the usual way. One would expect the oil thus obtained to be a mixture of diphenyl (from acid V), and of isopropyldiphenyl. This mixture was oxidized in pyridine solution with potassium permanganate exactly in the way described above for retenequinone. After the oxides of manganese and neutral matter had been removed, the alkaline solution was acidified and extracted with ether. The acid thus obtained was 3-diphenylcarboxylic acid. This completes the evidence for the constitution of retene by showing that the isopropyl group is in position 2- as represented in formula III. As this evidence, based especially on the formation of the two isomeric benzenetricarboxylic acids, 3-hydroxyisopropyl-1,1',2'-diphenyltricarboxylic acid and 3-diphenylcarboxylic acid *directly from retene*, is independent of all previous work we now have very strong evidence that the above structure must be correct.

The constitution of retene having been established, it is now an easy matter to correct the various structural formulas of the retene derivatives which appear in the literature. This includes compounds of diphenyl, diphenyleneketone, fluorene, reteneketone, retenequinone, etc.

Many important natural products are hydrogenated derivatives of retene. This is true especially of resin and resin oil derived from the *Coniferae* as is shown by many investigations, among which may be mentioned that of Schultze.[1] The mineral resin fichtelite, $C_{18}H_{32}$, is a completely reduced retene. It is therefore tetradecahydro-8-methyl-2-isopropylphenanthrene. The resin left from the distillation of turpentine is said to consist very largely of abietic acid. This acid is claimed to be a decahydroretenecarboxylic acid $C_{18}H_{27}.CO_2H$ and it is therefore not surprising that its hydrocarbon, $C_{18}H_{28}$ should occur in resin oil.

That abietic acid has the above constitution was apparently shown by Easterfield and Bagley[2] who succeeded in converting it into retene and also into dehydrofichtelite $C_{18}H_{30}$. As the acid has a low esterification velocity, they conclude that it is a diortho-substitution product. The formula of Bamberger and Hooker (I) for retene does not allow such a structure and they consider it incorrect in consequence. They then change the isopropyl group to position 6- and write the formula as follows (VII).



VII.

---

[1] *Ann.*, 359, 129 (1908).

[2] *J. Chem. Soc.*, 85, 1238 (1904).

Their formula would make retene an 8-methyl-6-isopropylphenanthrene. They offer no better evidence for their formula than Bamberger and Hooker did for formula I. They state that the formula is in accordance with the oxidation products, 1,2,4-benzenetricarboxylic- and metaphthalic acids! The very formation of these acids, however, is conclusive evidence against the formula, for such a compound would not yield the above acids. Their assumption is also shown to be untenable by the work described in this paper. It does explain the low esterification velocity of the acid, but many other arrangements would do just as well.

It may be pointed out that the formula (III), which has now been proved for retene, has *one* position (1-) diortho-substituted and if abietic acid is really a carboxyl derivative, the acid group might be in this position. The very extensive literature is so contradictory that one can not rely on it to decide this point. Some consider the abietic acid to be a dihydroxy derivative and others even question the composition, $C_{19}H_{28}O_2$, of the acid.

The wide bearing of the work, on retene, on natural products is still further shown by the suggestion of Neuberg and Rauchwerger that cholesterol is related to abietic acid and may therefore contain a reduced retene nucleus.

Brown University, Providence, R. I.

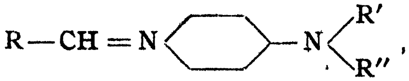
THE COLORED SALTS OF SCHIFF'S BASES.

III. THE SALTS OF BASES FORMED BY CONDENSING *m*-AMINODIMETHYLANILINE AND *m*-AMINODIETHYLANILINE WITH AROMATIC ALDEHYDES.

By F. J. Moore.

Received January 19, 1910.

It has already been shown in previous papers[1] that benzylidene compounds of the general type,



when treated with acids in non-aqueous solvents, add successively two molecules of the latter, and that the salts containing one molecule of acid differ markedly in color from those containing two molecules. The former are, for the most part, dark red, while the latter are light yellow, the free bases themselves varying from a light cream color to orange. For this behavior three possible explanations have been suggested. For a detailed discussion of these, the reader must be referred to the papers mentioned. Here it will be sufficient to sum them up briefly as follows:

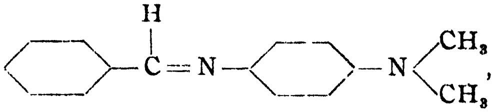
The first ascribes the difference in the color of the salts to the position of that nitrogen atom selected by the first molecule of acid. The second assigns to the dark-colored salts a quinoid constitution, regarding the compounds of lighter color as benzoid. The third assumes the potential existence of stereoisomeric red and yellow bases and salts, whose relationship to each other is akin, perhaps, to that of the isomeric unsymmetrical oximes.

---

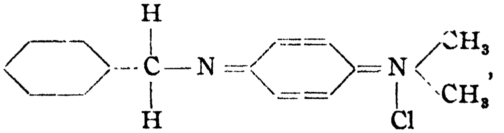
[1] This Journal, 30, 394 and 1001.

The work described in the present paper was undertaken with the intention of testing the second of these explanations, which regards the dark-colored substances as quinoid. In accordance with this hypothesis, the addition of hydrochloric acid to benzylidene-*p*-aminodimethylaniline, for example, would cause transformations such as are illustrated by the following series of formulae:

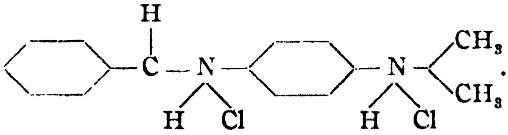
(1)



(2)



(3)



A convenient method of testing this hypothesis would consist in preparing analogous compounds which, from their structure, could not readily assume a quinoid constitution, and testing the results of salt formation in these cases. Now it is well-known that *p*-quinones form with considerable readiness, whereas *o*-quinones are more difficult to prepare, and *m*-quinoid substances are not known with certainty.[1] Applying this reasoning to the case in hand, it might be argued that the bases previously used in the course of this investigation might well form quinoid salts, since they all had their two nitrogen atoms in *p*-position to each other. It might, however, be confidently expected that the analogous *m*-compounds could not do this. Should these bases, when prepared, show a behavior with acids which was different from that of the *p*-compounds, then it might well be concluded that the dark-colored salts of the latter were quinoid. Should the *m*-compounds, on the other hand, show the same behavior as the *p*-compounds, then one of two possible conclusions might be drawn: either that the dark-colored salts of the *p*-compounds were not quinoid, or else that *m*-quinones may be formed more readily than any other evidence has thus far led us to believe.

---

[1] Compare R. Meyer, *Ber.*, 41, 2437; Zincke and Schwabe, *Ber.*, 42, 797; R. Meyer and Desamari, *Ber.*, 42, 2809.

The compounds first selected for the experimental investigation were the products formed by condensing *m*-aminodimethylaniline with aromatic aldehydes. The reaction takes place readily and smoothly. When the products were treated with hydrochloric acid in ethereal or benzene solution, all the salts formed proved to be light in color, the shade not being markedly different, whether base or acid was in excess. The greatest difference of this kind was shown by the condensation product with cinnamic aldehyde, which gave a decidedly redder precipitate when acid was in excess, than under the reverse conditions. It will be noticed that this behavior was entirely different from that of the corresponding *p*-compounds. On its face, this would seem to indicate that the dark-colored salts of the latter were quinoid. Unfortunately this argument is a good deal weakened by the curious physical properties of the bases themselves.

While the *p*-compounds crystallize beautifully from alcohol and other organic solvents, and have sharp melting points which make them useful for the identification of aldehydes, the condensation products of *m*-aminodimethylaniline with aldehydes have properties, which are the reverse of all this. They are typically amorphous, they crystallize from no solvent yet tried, and they have no melting point, but soften gradually on heating. They are, for the most part, very soluble in benzene, and on evaporation of this solvent, they are left as transparent resins which show no signs of crystallization even after months of standing. The products form readily when aldehyde and amine are mixed, and the yield is good. Side-reactions do not seem to take place, and when pains are taken to purify the products as far as possible, the analytical results agree well with the formulae derived from the method of preparation. Apparently then, the properties just described must belong to the compounds as such, although, of course, the usual criteria of purity are lacking. These properties would seem to indicate that the substances concerned were polymers, and if this were the case, the possibilities of constitution which have been thus far discussed might have little bearing. It seemed desirable to test this point by means of molecular weight determinations. Freezing-point measurements were therefore attempted in both benzene and diphenylamine. The substance chiefly studied was benzylidene-*m*-aminodimethylaniline, because it was believed that the sample used was purer, perhaps, than any of the other bases. A series of tests was, however, made with each of the other compounds. The results were discordant and unsatisfactory, the numbers obtained sometimes differing among themselves by a figure corresponding to a whole unit formula. Nevertheless the sum total of the results would seem to show that the bases were not high polymers. Speaking generally they indicate that in 0.5 per cent. solution, the bases were bimolecular. The association seemed to increase with increasing concentration, and in a 2 per cent. solution, the compounds appeared to have a molecular weight three or four times that represented by the simple formula. These results cannot be called satisfactory or conclusive, but are, perhaps, as much as can be expected from materials whose purity and homogeneity is open to so much question.

Since in any case the results above described gave no satisfactory solution to the original problem, *m*-aminodiethylaniline was prepared and condensed with five of the more common aldehydes. These compounds, in their turn, showed the same properties which have been already described as characteristic of the methyl compounds. They, too, are amorphous waxes or gums, and their salts are, for the most part, of light color, whether one or more molecules of acid are added.

Although both these bases have proved a disappointment so far as that problem is concerned for the solution of which they were originally prepared, yet their uniformly amorphous character when compared with the crystalline nature of the isomeric *p*-compounds suggests that their study might throw some light upon the fundamental differences which exist between the *m*- and *p*- relationships in di-substituted benzene derivatives. It is hoped to extend this study further in the future.

Experimental Part.

The *m*-aminodimethylaniline used in this investigation was prepared by the method of Groll[1] from dimethylaniline. The directions are easy to follow, and the product obtained is of satisfactory purity. When distilled in hydrogen, it boils with perfect constancy at 267° to almost the last drop.

From the literature, it is easy to get the impression that the aminodimethylanilines are unstable compounds. This is not the case, but they are extremely sensitive to the oxygen of the air. Indeed they turn black and grow tarry even on standing a few days in a well-stoppered bottle. If, however, they are distilled in hydrogen, and then the connections are hermetically sealed without allowing any access of air, no deterioration takes place. Samples which were treated in this way have been preserved in this laboratory for more than two years, and show no signs of change.

Benzylidene - m - aminodimethylaniline. — Molecular quantities of *m*-aminodimethylaniline and benzaldehyde were mixed. Condensation took place with a slight evolution of heat in the course of a few minutes, the mass becoming thick and pasty. To free the product from any possible excess of the amine or aldehyde, it was warmed several times with small portions of dilute alcohol (in which it is not very soluble), the pasty mass being constantly stirred to bring all parts of it into contact with the solvent. During this treatment, the substance assumes the consistency of a thick paste which can be drawn out like molasses candy into long golden-yellow strings. After several treatments of this kind, the substance grows hard and brittle on cooling. When this point had been reached, it was pulverized and washed with cold dilute alcohol. Finally, enough cold 95 per cent. alcohol was employed to bring the residue into solution, and this solution was poured into a large quantity of cold water. This causes a milky turbidity, but if a little sodium chloride solution is added, the substance is precipitated in flocks, which may then be rapidly filtered by suction and washed repeatedly with cold water. This latter method of purification was twice repeated, and the product finally dried in vacuum. It was now a light yellow mass which retained hardly any odor of benzaldehyde, and when pulverized was extremely electric. No crystalline form could be observed in this product, and all attempts to find a solvent from which it would crystallize have proved fruitless. Nevertheless the following results of analysis seem to show that the substance was essentially pure benzylidene-*m*-aminodimethylaniline.

---

[1] *Ber.*, 19, 200 (1886).

Calculated for $C_{15}H_{16}N_2$:	C, 80.30;	H, 7.19;	N, 12.52.
Found:	79.97;	7.20;	12.69.

Condensation Products with Other Aldehydes.—*m*-Aminodimethylaniline was also condensed with anisaldehyde, cinnamic aldehyde, and piperonal. All the products had essentially the same properties as that just described. For this reason, the details need not be repeated. Purification was also carried out in the same manner where this was possible, but the method of dissolving in alcohol and precipitating by water did not work well in the cases of the cinnamic aldehyde and piperonal compounds. It is therefore probable that these compounds were not as pure as the others. This is also borne out by the results of analysis. Only nitrogen determinations were made in these cases.

Anisylidene-m-*aminodimethylaniline*: Calculated for $C_{16}H_{11}ON_2$, N 11.05; found, 10.91.

Cinnamidene-m-*aminodimethylaniline*: Calculated for $C_{17}H_{18}N_2$, N 11.23; found, 9.96.

Piperonylidene-m-*aminodimethylaniline*: Calculated for $C_{16}H_{16}O_2N_2$, N 10.45; found, 9.04.

Derivatives of m-*Aminodiethylaniline.*—The *m*-aminodiethylaniline required was prepared essentially according to the suggestions of Groll[1] by nitrating diethylaniline and reducing the *m*-nitro compound. Groll's directions for the nitration and separation of the *m*- and *p*-products can hardly be improved. From reading his article, however, one gets the idea that the *m*-nitro compound can be distilled at ordinary pressure. Attempts made to do so in this laboratory yielded a product much contaminated by water and some ill-smelling substance whose odor resembled that of pyridine. This nitro compound can however be obtained in a high state of purity by distilling with steam. At 100° this process is very slow and tedious, and the quantities of water required are so large as to render the subsequent ethering-out very laborious. Much better results are obtained when the flask containing the nitro compound is placed in an oil bath heated to 160° (thermometer in the bath) and superheated steam then blown through. In this way, no water condenses in the distilling flask, and a liberal quantity of very pure oil distils over rapidly. Small amounts of this nitro compound can be conveniently identified by the precipitate obtained at once when it is treated with picric acid in alcoholic solution. After a single crystallization from alcohol, this picrate melts at 138° (uncorrected).

---

[1] *Loc. cit.*

Reduction to the amino compound proceeds very smoothly under the influence of tin and hydrochloric acid. The most convenient method of isolation is to pour the hot reduction mixture directly into an excess of concentrated caustic soda solution, warm a few minutes, cool with an equal quantity of ice, and shake out with ether. A second treatment with ether is superfluous. In this way, 75 grams nitro compound yielded 50 grams amine which, when distilled in hydrogen, boiled constantly at 277°. The freshly distilled base is as nearly colorless as freshly distilled aniline, and consequently somewhat purer than that described by Groll. Like other substances of its class it is very sensitive to the air, rapidly turning brown. Portions of it which are not intended for immediate use should therefore be at once sealed up in an atmosphere of indifferent gas. When an alcoholic solution of the base is mixed with picric acid, no precipitate forms at once, but after standing for some time, beautiful yellow prisms separate. These can be washed repeatedly with cold alcohol, and then recrystallized from the same boiling solvent. They then melt sharply at 152°.

Condensation Products with Aldehydes.—These compounds were prepared in the same manner as the analogous methyl compounds. A general account of their physical properties has already been given in the earlier portion of this paper. These properties made it so evident that no assistance could be obtained from them, in solving the question at issue, that no thorough study was made of them, and no analyses carried out. A brief account of their appearance and the color of their addition products with hydrochloric acid follows.

The condensation products with benzaldehyde and anisaldehyde are stiff, golden yellow gums. When they are dissolved in ether, and an ethereal solution of hydrochloric acid is added, the precipitate first thrown down is pale yellow. This becomes practically white when an excess of the acid is added.

The compound formed with cinnamic aldehyde is a brick-red pasty mass. It also is soluble in ether, and from this solution hydrochloric acid precipitates a flocky red salt.

The condensation product with piperonal is a greenish yellow slime. When hydrochloric acid is added to its solution in dry ether, the precipitate first formed is pale yellow. A little more acid changes this color to a light red, and an excess to a bright lemon-yellow.

The compound formed with vanillin is a dark, blood-red, transparent jelly. Hydrochloric acid precipitates yellow salts.

Summary.

The salts of bases formed by condensing *m*-aminodimethylaniline and *m*-aminodiethylaniline with aldehydes do not show the same peculiarities of color as the corresponding salts of the *p*-compounds.

From this the conclusion might be drawn that the dark-colored salts of the latter were quinoid, but the force of this argument is a good deal weakened by the probability that these *m*-bases are polymers.

The amorphous character of these compounds (perhaps due to polymerization) in contrast to the crystalline nature of the *p*-compounds suggests applications to the benzene problem which are worthy of future study.

The thanks of the writer are due to Mr. E. G. Genoud for much valuable assistance during the earlier portions of this work.

MASS. INST. TECHNOLOGY, BOSTON, MASS.

THE ACTION OF MAGNESIUM UPON THE VAPORS OF ORGANIC COMPOUNDS.

BY EDWARD H. KEISER AND LEROY MCMASTER.

Received January 18, 1910.

In 1894 Edward H. Keiser and M. B. Breed[1] studied the action of metallic magnesium upon the vapors of some of the aliphatic alcohols and found that when the metal is heated in a tube through which the vapor of the alcohol is passing it soon begins to glow and after the action has ceased and the tube allowed to cool, a black residue is left. This residue when put into water evolves a gas slowly and on the addition of a few drops of ammonium chloride a more rapid evolution of gas is obtained. It was shown that the gas thus given off consisted of hydrogen mixed with small quantities of allylene.

In a subsequent paper by Edward H. Keiser[2] the work was continued, other alcohols and acetone were subjected to the action of magnesium, and it was shown that in every case the black residue gave off allylene when treated with water. The best yield of allylene was obtained from the black mass formed by the action of magnesium upon acetone. It was also shown that when magnesium is heated in an atmosphere free from hydrogen, as for instance, in carbon monoxide and carbon dioxide, a very hard compact black mass is obtained which gives only small quantities of allylene on treatment with water. The conclusion was, therefore, drawn that a magnesium compound of allylene was probably present in the black residue.

---

[1] *J. Franklin Inst.*, Dec., 1894.

[2] *Am. Chem. J.*, 18, 328.

We have now endeavored to determine whether a magnesium compound of allylene or simply a carbide of magnesium is present in the black residue. In the earlier experiments several of the aliphatic alcohols, allyl alcohol and acetone had been acted upon by the magnesium; we now extended the work so as to include other classes of compounds such as paraffin and aromatic hydrocarbons, aliphatic acids and esters, aromatic alcohols, halogen derivatives, acetylene, cyanogen, etc.

The method of operating was the same as before, the metal in an iron boat was placed in a combustion tube of glass, the tube was heated in a small furnace and the organic compound was passed through the tube in the form of vapor. After the action was over the black magnesium residue was allowed to cool off in the vapor. The black residue was then put into a dry evolution flask provided with a separatory funnel and water containing a few drops of ammonium chloride was allowed to drop upon it. The gases evolved were passed into an ammoniacal solution of silver nitrate. The silver precipitates thus obtained were analyzed. The following table (see p. 390) contains the results of these analyses.

These results show that in every case when magnesium is heated in the vapor of a compound containing hydrogen the unsaturated hydrocarbon evolved from the black residue is chiefly allylene. When hydrogen is absent, as in the cases of cyanogen and carbon monoxide a very poor yield of unsaturated hydrocarbon is obtained, four to five times as much of the black magnesium residue must be used in order to obtain sufficient of the silver precipitate for analysis. The analytical results show that even in these cases the gas evolved is not pure acetylene but contains some allylene. Thus from cyanogen the silver precipitate was found to contain but 82.95 and 82.72 per cent. of metal whereas pure silver acetylide contains 89.9 per cent.; and in the case of carbon monoxide the silver precipitate gave 78 per cent. of silver. These low results indicate a mixture of allylene and acetylene and at first thought it would appear that a carbide of magnesium is formed in all these experiments and that the allylene is formed by the action of water upon this carbide. This conclusion would be justified were it not for the fact, noted in the earlier paper, that magnesium powder contains hydrogen, either as occluded hydrogen, or hydroxide or both. This has been proved by burning weighed amounts of magnesium powder and weighing the water formed.

The average result of two combustions of magnesium powder, previously dried for several hours at 120° in an air bath, gave 0.065 per cent. of hydrogen.

ANALYSES OF SILVER PRECIPITATES.

Magnesium allylide from	Weight taken.	Wt. AgCl found.	Per cent. Ag.
n-butyl alcohol (*a*)	0.1281	0.1262	74.16
(*b*)	0.1422	0.1388	73.48
Benzyl alcohol	0.2715	0.2661	73.81
Ether	0.1271	0.1240	73.44
Ethyl bromide	0.0554	0.0543	73.78
Benzyl chloride	0.0898	0.0894	74.90
n-butyric acid	0.0336	0.0328	73.48
Isobutyric acid	0.1210	0.1190	74.30
Ethyl acetate (*a*)	0.1042	0.1038	74.96
(*b*)	0.0815	0.0812	74.98
Isobutyl acetate (*a*)	0.1534	0.1496	73.42
(*b*)	0.1447	0.1419	73.78
Amyl acetate (*a*)	0.1423	0.1388	73.43
(*b*)	0.1051	0.1027	73.53
Hexane	0.0400	0.0384	72.24
Benzene	0.1067	0.1062	74.81
Kerosene (*a*)	0.0418	0.0417	75.11
(*b*)	0.0599	0.0595	74.76
Illuminating gas (*a*)	0.1370	0.1384	76.05
(*b*)	0.1504	0.1522	76.17
(*c*)	0.1290	0.1260	73.51
(*d*)	0.1311	0.1280	73.50
(*e*)	0.2340	0.2285	73.51
Cyanogen (*a*)	0.1027	0.1132	82.95
(*b*)	0.0637	0.0700	82.72
Acetylene (*a*)	0.3213	0.3590	84.10
(*b*)	0.1854	0.2063	83.80
Carbon monoxide	0.0818	0.0851	78.20
CO and nitrogen	0.0787	0.0814	77.83
CO + N_2 + HCl	0.0550	0.0547	74.80
Calculated for silver allylide, AgC_3H_3			73.45

This fact of the presence of hydrogen in the magnesium and the other fact that only a very small amount of the unsaturated hydrocarbons is obtained from carbon compounds containing no hydrogen led us to conclude that magnesium allylide is present in the black residue. There is undoubtedly a tendency on the part of magnesium, under the conditions of our experiments, to combine with carbon and hydrogen to form magnesium allylide and it is this compound which with water evolves allylene. This is shown clearly in the case of the experiments with acetylene. When magnesium powder is heated in this gas a black residue is obtained which with water gives off both allylene and acetylene. Here the conditions were favorable for the formation of only a carbide, as MgC_2, yet the gas given off consists of both hydrocarbons. Further, when carbon monoxide, diluted with nitrogen to make the action less violent, was acted upon by magnesium, the black residue gave very little silver precipitate, but when hydrochloric acid gas was added to the mixed gases then a good yield of unsaturated hydrocarbon was obtained and the analysis of the silver precipitate indicated nearly pure allylene. We conclude, therefore, that it is magnesium allylide that gives the allylene and not a carbide.

CHEMICAL LABORATORY, WASHINGTON UNIVERSITY,
ST. LOUIS, MO

STUDIES IN THE ACTION OF HEAT ON MILK.[1]

BY R R. RENSHAW AND F. C WARE.

Received January 11, 1910.

A number of experimenters[2] have noticed that when milk is heated, the lactose apparently diminishes in quantity. The subject, however, has not been systematically investigated.

Richmond[3] first called attention to the fact that the specific rotatory power of lactose in milk materially diminished on heating, but that the reducing power decreased only slightly. Later he and Boseley[4] determined lactose in samples heated for $1^1/_2$ to 3 hours at 100° and found that there was a decrease of from 8.8 per cent. to 23 per cent. of the sugar as measured by the optical method. In another series where sugar was determined gravimetrically, no change was noticed. They offered the suggestion that this may be due to the formation of caramel, since the rotatory power decreased roughly in proportion to the increase of yellow color in the milk.

It did not seem to the present authors that caramelization could be the primary cause of the difference in the optical and gravimetric determinations, since the rotatory and reducing power should decrease nearly proportionally, due to the relatively large molecule of the caramel compared to that of lactose. It was for the purpose of investigating this that the following experiments were undertaken. We were particularly interested to find out the character and extent of the change taking place at the temperatures which might be used in pasteurization.

A number of possible causes for the change in rotatory power of the milk serum presented themselves among which may be mentioned changes producing soluble *l*-rotatory glycerophosphates,[1] or small amounts of a highly *l*-rotatory amino acid, not precipitated by the clarifying agents used. In order to test these, the sugar was determined by both methods, as well as total phosphorus and total nitrogen in the protein-free serum, on samples of milk heated different lengths of time up as high as 80°. A rapid decrease of sugar was noticed, but strange to say nearly identical results were obtained by each method, and in all subsequent work concordant results were obtained where great care was used in maintaining uniform conditions, particularly as to temperature of pipetting samples,[2] complete washing of the asbestos filter, etc. With such results from the preliminary experiments it was thought not necessary to consider phosphorus and nitrogen determinations.

---

[1] Submitted by F. C. Ware, in partial fulfilment of the requirement for the degree of Master of Arts at Wesleyan University, June, 1908. The experimental work was carried on in the Chemical Laboratory, Stamford High School, Stamford, Conn.

[2] Wroblewski, *Oest. Chem. Ztg.*, **1**, 5 (1898); Leeds and Coon, *Pharm. J.*, **23**, 86; Cazeneuve and Haddon, *Compt. rend.*, **120**, 1272; and others.

[3] *Analyst*, **17**, 222.

[4] *Ibid.*, **18**, 141 (1893).

We next took up a study of the behavior of lactose in a solution which contained approximately the same active mass of hydroxyl ions that occur in milk, in order to see if the alkaline salts were instrumental in the decomposition. Owing to the great complexity of milk as a solution, with its varying amounts of di- and triatomic acids and bases, each with a different temperature coefficient of ionization, and to the incalculable chemical changes caused by heat, it is impossible to compute ionic concentrations. Practically, however, an approximation could be obtained easily, by making a solution containing equivalent percentages of the principal electrolytes found in milk, with the understanding that precipitation of solids and evolution of carbon dioxide would occur. For this purpose 1 gram each of hydrochloric and citric acids,[3] 2.42 grams phosphoric acid, and calcium carbonate containing 1.9 grams of calcium oxide, were mixed with water and the solution neutralized to phenolphthalein with 0.1 *N* sodium hydroxide and 148 cc. (alkalinity × 10) in excess added. In this, 4.87 grams of lactose were dissolved and the whole made up to a liter, giving a solution containing one-tenth of the percentage of sugar that was found in the milk we were working with. No change in sugar content was noticed after heating this for two hours and a half at 85°. This solution, containing approximately the same amounts and similar kinds of positive and negative elements or radicles as occur in milk, except, of course, that all were in inorganic combination, should afford as high, if not a higher, hydroxyl ion concentration than the milk. It seemed then that the salts had no effect on the sugar at this temperature.

Series of tests were next run on milk heated to 60, 70, 80, and 85°. Three sets of samples were made up for each temperature from the same specimen. One of pure milk, the second containing formaldehyde, 1 : 2500, and the third the same, 1 : 20000. The aldehyde was used in these two concentrations in the hope of distinguishing between bacterial and enzymatic action.[1]

---

[1] Bordas and Raczkowski (*Ann. chem. anal.*, 8, 168 (1903)) have shown that when milk is heated the lecithins are decomposed.

[2] It was noticed that temperature differences materially affected results. The analytical work was done in a room fitted up with a constant temperature regulator.

For sugar, the Wiley and Erwell optical and the Defren gravimetric methods were used. The acidity was determined with phenolphthalein without the removal of carbon dioxide and is expressed below in cc. of 0.1 *N* sodium hydroxide per 100 cc. milk. Lacmoid was used for alkalinity. It also is expressed in cc. 0.1 *N* solution per 100 cc. milk.

The presence of a sediment containing calcium phosphate was confirmed in the pasteurized milk.

The sugar, acidity and alkalinity were determined immediately after cooling the sample. The milk used in the 70 and 80° tests was of the same lot, from a mixed herd, and was about five hours old at the beginning of the 70° test. That for the 80° test stood about four hours longer in a good refrigerator. The tests at 60 and 85° were run about a month later on milk from the same dairy and at about the same length of time after milking.

The results for 60 and 80° are given below in detail:

RESULTS ON MILK HEATED AT 60°.—LACTOSE.

Time heated.	0 hr.	¼ hr[2]	½ hr.	¾ hr.	1 hr.	1½ hrs.	2 hrs.	2½ hrs.	Diff.
Milk alone, opt.	4.42	4.34	4.3	4.27	4.24	4.13	4.02	3.96	0.46
Milk alone, grav.	..	4.32	. .	4.26	.....	4.11	.....	3.96	0.49
" and ald. 1 : 2500, opt.	. . .	4.37	4.35	4.35	4.34	4.32	.....	4.33	0.09
" and ald. 1 : 20000, opt.	....	4.39	....	4.37	.....	4.25	.....	4.24	0.18
Acidity	21.4	22.0	22.5	22.8	23.4	24.5	25.6	26.0	4.6
Ald. 1 : 2500	.....	21.6	21.4	21.6	21.8	21.7	21.8	22.0	0.6
Ald. 1 : 20000	.....	21.8	.....	22.2	.....	22.6	.. ..	22.7	1.3
Alkalinity	31.4	30.4	29.9	29.6	29.2	28.6	28.2	27.6	3.8
Ald. 1 : 2500	.....	31.2	31.24	31.0	31.2	30.8	31.0	30.78	0.62
Ald. 1 : 20000	.....	30.9	.....	30.6	.. ..	30.2	.....	30.0	1.4

RESULTS ON MILK HEATED AT 80°.—LACTOSE.

Time heated.	0 hr	¼ hr	½ hr	¾ hr.	1 hr.	1½ hr	2 hr.	2½ hr.	Diff.
Milk alone, opt.	4.52	4.37	4.21	4.08	4.05	4.01	4.0	4.0	0.52
Milk alone, grav.	4.48	4.33	4.17	4.07	3.98	3.96	3.97	3.96	0.53
Ald. 1 : 2500, opt.	.....	4.48	.....	4.46	.. .	4.47	.....	4.44	0.08
Ald. 1 : 20000, opt.	.....	4.46	.....	4.44	.....	4.41	.....	4.41	0.09
Acidity	16.8	18.4	19.5	20.3	20.7	21.3	21.8	21.7	4.9
Ald. 1 : 2500	.....	16.9	.....	17.0	.....	17.1	.....	17.2	0.4
Ald. 1 : 20000	.....	17.1	.....	17.2	.....	17.6	.....	17.7	0.9
Alkalinity	33.4	32.1	31.4	30.9	30.5	30.1	29.5	29.2	4.2
Ald. 1 : 2500	.....	33.4	.....	33.2	.....	33.0	.....	32.9	0.5
Ald. 1 : 20000	.....	33.2	.....	33.4	.....	32.7	.....	32.5	0.9

[1] Price (*Abs. U. S. Hyg. Lab., Bull.* 41, 379) has shown that many enzymes can withstand formaldehyde 1 : 20000, while the growth of the more common bacteria is prevented. A strength of 1 : 2500 stops the action of most enzymes.

[2] This does not include the time of heating necessary to bring the milk up to the required temperature in the thermostat but means 1/4 hr. at the designated temperature. For the 85° test this required 15 minutes and for the lower temperatures a somewhat shorter time.

In the series at 60°, a fairly regular and continuous decrease was noticed up to $2^1/_2$ hours in the sugar and alkalinity, while there was a corresponding increase of acidity. Practically no changes occurred in the sugar and acidity when formaldehyde was present in the proportion of 1 : 2500, and only slight changes with a strength of 1 : 20000. At 80° the changes were more rapid at the beginning and had nearly ceased by the end of the first hour. Figures obtained at 70° showed that the changes here stood intermediate between the two given. At 85° the changes went more rapidly at the beginning and were practically over after the first $^1/_2$ hour. There was neither as much decrease in sugar or alkalinity, nor as much increase in acidity, however, as in the case of the lower temperatures.

It would seem then that the major cause of the change in the sugar was bacterial or enzymatic action, for, although no very strict relationship seems to exist between the amount of acid formed and the decrease of sugar, as the following table exhibits, still, the results are in accord with Haacke's[1] observation that the amount of lactic acid found at any one time is not strictly proportional to the amount of lactose decomposed, because (probably) the lactic acid is transformed into other substances. The acid never exceeds one-third of the amount of sugar decomposed.

	60°	70°	80°.	85°
Per cent. sugar loss after $2^1/_2$ hours .	10.4	11.94	11.28	6.33
Increase of acid calc. as gs. lactic .	0.0414	0.0513	0.0441	0.0333
Loss of lactose in gs	0.46	0.54	0.52	0.28

It is difficult to interpret in the light of our results, the data found in the literature showing the differences in optical and gravimetric determinations for sugar in heated milk, because the temperatures used were higher (100°), and neither the history of the milk nor the details of analysis were given. We regret that time has not permitted investigating the sugar changes at 100°. It seems certain, however, that the data furnished by the difference between the optical and gravimetric methods for sugar in pasteurized milk cannot be used as confirmatory evidence of pasteurization, as has been recommended.

Theoretically, of course, very different results would be obtained from different samples of milk, due to varying amounts (as well as kinds) of inoculation, for it has been shown that the lactic acid organisms vary greatly in the extent, rapidity and persistency of their action. Tissier and Gasching[2] state that *B. acidi-paralactici* has a high order of resistance, that it works actively and vigorously, and produces mostly *d*-lactic acid. Heinemann[3] seems to have shown that ordinary *B. acidi-lactici* gives chiefly the *l*-acid, and this appears to be augmented by higher temperatures.[1]

---

[1] *Arch. Hyg.*, 42, 16–47 (1902).

[2] *Ann. inst. Pasteur*, 17, 540–563 (1903).

[3] *J. Biol. Chem.*, 2, 603–612 (1907).

Observations by Rullman,[2] that it requires an hour's heating at 68–69° to kill the major portion of the bacteria in milk, and by Mullen,[3] that oxidizing ferments increase in activity from 0 to 60°, and that they are still active at 80°, are noteworthy. The investigations of many others[4] support the statement that the milk ferments are not materially injured by heating at 60–65° for some time. They are weakened only at 65–70° and are finally destroyed at 70–80°.

These facts, along with the knowledge recently obtained concerning the action of Metchnikoff's *B. bulgaricus*, largely remove the cause for surprise at the large amount of sugar transformed. It has been shown that *B. bulgaricus* is universally found in milk. It works best at temperatures above 40° and under the anaerobic conditions which would prevail, at least in bottle pasteurization, and it propagates prodigiously, producing extraordinary amounts of lactic acid. It is hence not necessary to assume cytolysis, with an accompanying liberation of an intracellular enzyme having a higher thermal death-point than the organism. It is to be regretted that so little work has been done in determining the important relation between the thermal death-points of the organisms and their characteristic enzymes.

From the small differences between the results obtained by using the two strengths of formaldehyde, it would appear that one was dealing with bacterial rather than enzymatic action. This is further substantiated by the fact that it is an exceedingly difficult matter to procure lactic acid enzymes from lactic acid organisms.[5] Such small differences as are observed might be due to only partial killing of the bacteria at the lower concentration, or to a slight secretion of an extracellular enzyme.[6] The very rapid transformation of sugar into lactic acid (in one case 0.24

---

[1] These facts indicate that for very close work certainty of complete precipitation of the lactic acid by the clarifying agents is necessary if the fermentation has occurred at higher temperatures, for under these conditions equivalent amounts of *d*- and *l*-acid may not be formed.

[2] *Z. Nahr.-Genussm.*, 7, 81–89 (1904).

[3] *Arch. Hyg.*, 44, 132–3 (1902).

[4] For a comprehensive review of this subject and for some original contributions, see article by Kastle and Roberts, *U. S. Hyg. Lab., Bull.* 41, 309–408 (1908).

[5] The senior author has attempted, so far unsuccessfully, to get a lactic acid enzyme from B. *acidi-lactici* in sufficient quantity to experiment with. It is hoped that this may yet be done. Herzog (*Z. physiol. Chem.*, 381 (1903)) got a very slightly active solution from this organism which would transform lactose into lactic acid in the absence of organisms.

[6] Dox, in a paper on "The Development of Catalase in Lower Fungi," read at the Boston meeting of the American Chemical Society, Dec., 1909, stated that he found a rise of temperature favored the formation of extracellular enzymes.

gram giving 0.0252 gram acid in $^1/_2$ hr.) seemed extraordinary to the authors. It has been abundantly proven, however, that there are optimum temperatures for catalyzers in general, that is, temperatures allowing a maximum in the reaction along with a minimum of destruction to the catalyzer itself.

Many instances could be cited of the extraordinary influence of rise of temperature on the reaction velocity of catalytic actions, and particularly is this true of organic catalyzers (enzymes) within narrow margins of temperature. For instance, Tammann[1] has found that the temperature coefficient for emulsin on salicin between 60 and 70° was 12.3. What is true of enzymes is also true in a degree of cells, for broadly speaking these also are catalyzers, or rather systems of catalyzers. The organisms, then, may continue very rapidly to increase in activity until finally they die in hyper-activity. With this in mind, the increased velocity of sugar decomposition as higher temperatures were used becomes clear. This affords an explanation, too, of the occasional curdling of milk on pasteurizing, and gives further reasons for using a not too highly inoculated milk in such processes.

Conclusions.

1. The alkaline salts have no effect on the lactose in milk when it is heated at 85° for some time.

2. Perfectly concordant results can be obtained by the optical and gravimetric methods for lactose in pasteurized milk.

3. Concordance between the results by the optical and gravimetric methods can not be taken, as has been suggested, as evidence that the milk has not been pasteurized.

4. In bottle pasteurization it is impossible to heat the milk quickly enough to prevent appreciable amounts of lactose being decomposed, unless the milk has a very small bacteria count.

5. Some lactic acid organism or organisms work prodigiously at a temperature of 80-85°, though for a short time. They work more slowly but for a longer time at 60°.

6. The presence of a sediment containing calcium phosphate in pasteurized milk has been confirmed.

WESLEYAN UNIVERSITY, MIDDLETOWN CONN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MICHIGAN EXPERIMENT STATION.]

ORGANIC NITROGENOUS COMPOUNDS IN PEAT SOILS.

BY S L. JODIDI

Received January 27, 1910.

When we take into consideration that not less than one-seventh of the total area of the state of Michigan consists of swamp lands largely covered by peat and muck, which is more or less also true of New England, of the northwestern, western and middle states, and that their entire area in the Union is estimated to reach the imposing figure of 75,000,000 acres, we are impressed with the necessity of an investigation of peat soils with a view to learning as much as possible about their agricultural possibilities.

---

[1] *Z. physiol. Chem.*, 16, 323.

As far as could be learned from the literature within our reach, no systematic investigations of a similar nature have been conducted.

When we consider a soil from the standpoint of agricultural chemistry, one of the first things to demand attention is the so called tripod of agriculture. This is natural enough, since many soils are deficient in one or more of the three essential elements: potassium, phosphorus and nitrogen.

Though the atmospheric ocean surrounding the earth contains countless millions of tons of nitrogen, it is, as such, of little avail, since the plants—with the exception of the legumes—are not able to utilize the free nitrogen of the air. It is the combined nitrogen only that is of agricultural value. Besides, there are a number of processes by which the nitrogen is liberated from the nitrogenous compounds and lost as plant food. The process of combustion, the denitrification through microorganisms, and the reaction of nitrous acid upon organic nitrogenous compounds, the spontaneous decomposition of ammonium nitrite liberate[1] more or less free nitrogen.

True, some combined nitrogen in the shape of nitric acid and ammonia comes with atmospheric precipitations into the soil which is still more enriched with nitrogen through the activity of certain soil bacteria. But it is certain that, to-day, a much larger amount of nitrogen is removed from the soil than is returned to it by synthetic or other means.

In the peat bogs, nature has placed at the command of man soils with large quantities of combined nitrogen. From the data given below, it will be seen that Michigan brown peat—the most abundant type in that state—contains in round figures from 2 25 to 2.75 per cent. nitrogen in the oven-dried state. This percentage means that about four tons of nitrogen are contained in each acre-foot. Such a quantity of nitrogen, if it could be utilized, would be sufficient for continuous cropping during three-quarters of a century. As far as inorganic nitrogen is concerned, it was found that nitrates are not present in the brown peat deposits occurring in Michigan; also that the quantity of ammonia present is quite small, ranging from a few thousandths to a few hundredths of one per cent. Hence the nitrogen practically consists of organic bodies only. But of what nature are they? This question seems to be quite a complicated one when we consider that organic nitrogenous compounds exist in the shape of amines, acid amides, monamino and diamino acids, cyanides, indole derivatives, pyridine derivatives, etc., and that a good many of these bodies can be of aliphatic as well as of aromatic origin.

---

[1] O. Kellner and T. Yoshii, *Z. physiol. Chem.*, 12, 105–107 (1888).

However, contemplations of a general nature will give us some idea as to the direction in which the problem under consideration can be attacked. It must be borne in mind that peat is a decomposition product of vegetable matter. Since the bulk of nitrogen in plants is commonly made up of proteins, which are contained in all plants, it is obvious that our attention must be directed first of all to the proteins and their decomposition products. However, in order to get some general conception as to the compounds or groups of bodies that may be present in peat, we must take into consideration the processes that take place in the plants when they cease to live. It is only protein in a dry state that is of a constant nature, but when subjected in a moist state to the influence of the ubiquitous bacteria—which is the case with protein in dead plants—it soon begins to decompose. The process of decomposition splits the complicated protein molecules into a considerable number of products. The following nitrogenous decomposition products have been discovered and identified by a great number of investigators:

Ammonia,[1] leucine,[2] tyrosine,[3] aminovaleric acid,[4] indole,[5] skatole,[6] indole acetic acid,[7] indole propionic acid,[8] putrescine,[9] cadaverine,[9] ptomaines generally, and others.

The nitrogenous decomposition products furnished by boiling the proteins with acids, *e. g.*, with hydrochloric acid, are as follows:

Ammonia,[10] histidine,[11] arginine,[11] lysine,[11] diamino-acetic acid,[12] glycocoll,[13] alanine,[13] aminovaleric acid,[13] leucine,[10] tyrosine,[10] aspartic acid,[10] glutamic acid,[10] cystine,[14] phenylalanine,[13] α-pyrrolidinecarboxylic acid,[13] oxyproline and humin substances.

Since peat has its origin from gradually decayed plants, and as far as nitrogen is concerned, chiefly from decayed proteins, it follows that the

[1] *Z. physiol. Chem.*, 22, 514–521 (1896–97).

[2] *Ibid.*, 22, 514 (1896–97).

[3] *Ibid.*, 2.

[4] E. und H. Salkowski, *Ber*, 16, 1191.

[5] W. Kühne, *Ber.*, 8, 206.

[6] M. Nencki, *Z. physiol. Chem.*, 4, 371–372.

[7] *Z. physiol. Chem.*, 9, 8–22 (1885); *Ber.*, 13, 189; *Z. physiol. Chem.*, 27, 302 (1889); *Ber.*, 37, 1801 (1904).

[8] E. Salkowski, *Z. physiol. Chem.*, 27, 302 (1899) *Ber.*, 38, 2884 (1905).

[9] A. Ellinger, *Ber.*, 31, 3183.

[10] Hlasiwetz und Habermann, *Ann.*, 169, 150; also *J. prakt. Chem.*, [2] 7, 397.

[11] E. Schulze und E. Winterstein, *Z. physiol. Chem.*, 28, 459.

[12] Drechsel, *Ber. sächs. Ges. Wiss.*, 44, 115.

[13] Emil Fischer, P. A. Levene und R. H. Aders, *Z. physiol. Chem.*, 35, 70–79 (1902).

[14] K. A. H. Morner, *Z. physiol. Chem.*, 28, 595 (1899).

series of bodies representing the decomposition products of proteins through the action of micro-organisms is of special interest to us. However, it is not out of the question that we may find compounds present in the peat which are generally associated with the decomposition of proteins by mineral acids.

By considering the above two series of decomposition products more closely, we can readily see that the great majority of them belong to two classes of organic compounds, namely to the monamino acids—leucine, tyrosine, aminovaleric acid, aspartic and glutamic acid, etc.—and to the diamino acids—histidine, arginine, lysine and diamino acetic acid. Some of the monamino acids, *e. g.*, the aspartic and glutamic acid may originate from the amides, asparagine and glutamine, which are, as such, often contained in plants. Thus we logically come to the conclusion that the bulk of nitrogen in peat may be present in the shape of amides, monamino acids, and diamino acids.

We must not omit to mention here that it is reasonable to assume that the plants, through the decay from which the peat resulted, may have contained also nitrogenous bodies other than proteins, and further, that decomposition in nature, under the influence of its various agents, may be in some respects different from the decomposition in the laboratory of proteins proper, either by chemical means or through bacterial activity. The possible interaction of the decomposition products and the leaching in nature must also be taken into consideration. Consequently, the separation of the peat constituents into amides, diamino acids and monamino acids may not take place exactly in the same manner as it does with proteins. This should be kept in mind by viewing the data presented in Tables III and V.

The method applied for the separation of the organic nitrogenous bodies in peat soils was essentially the one employed in protein chemistry with slight modifications. A definite volume of the sulphuric acid or the hydrochloric acid extract of peat, corresponding to, say, 0.05 gram nitrogen was, after cooling, carefully neutralized with cream of magnesia, of which some excess was used. The ammonia obtained by distillation gave the amount of nitrogen corresponding to the amides present in the peat.

The residue from distillation with magnesia was dissolved in dilute sulphuric acid so as to have approximately a five per cent. acid solution, then phosphotungstic acid solution added in some excess and allowed to stand for at least twenty-four hours. The precipitate containing the diamino acids was then filtered out, washed with water containing from two and one-half to five per cent. sulphuric and the same amount of phosphotungstic acid. The filter, together with the diamino acid precipitate, was transferred to a flask and the diamino nitrogen estimated according to Kjeldahl's method.

The filtrate and washings from the diamino acids, containing the monamino acids, were filled up with distilled water to a definite volume, usually to 500 cc., of which 100 cc. or 200 cc. were oxidized by the Kjeldahl method. The amount of ammonia found by distillation and calculated to the total volume gave the percentage of nitrogen corresponding to the monamino acids.

Instead of directly determining the amount of monamino nitrogen by Kjeldahl's method, which is difficult to accomplish in an exact way, the sum of the percentages of amido nitrogen and diamino nitrogen can be subtracted from the total quantity of nitrogen extracted from the peat. The difference evidently represents the monamino nitrogen.

Experimental Part.

Prior to starting experiments with the object in view of finding out the various organic nitrogenous compounds contained in peat soils, it was thought advisable to establish their composition by elementary analysis. This was also suggested by the fact that the literature, as far as we know, contains very few complete analyses of American peat soils, at least as far as the organic constituents are concerned. The brown peat sample,[1] the analyses of which are given below, is one that is typical for Michigan. It was taken from three to four feet below the surface or about the usual water-line in that peat deposit. It was made up of fibrous remains of sedges and, in the upper layers, of small shrubs and similar plants. It represents a well-decomposed, fibrous, brown peat. In order to have the peat sample in a state suitable for analytical purposes, it was dried in an electric drying oven at a temperature of from 40 to 60°, and then put through a 20-mesh sieve.

Calculated to water-free basis, the analysis gave:

C, 55.06; H, 5.21; N, 2 74; S, 0 35; Ash, 6 62; O (by difference), 30.02.

In order to be able to separate the nitrogenous bodies present in peat soils, it was necessary first of all to find a suitable solvent for the extraction of these compounds. It was soon found that the quantity of nitrogenous substances which could be extracted with water was small. Moderately dilute hydrochloric and sulphuric acids proved to be the most suitable solvents for the purpose we had in view. Since only a small part of the peat soils could be dissolved in these acids, the suggestion was plausible that a number of factors, like the amount and concentration of the acids, temperature and duration of digestion, as well as the fineness of the samples, might have an influence upon the percentage of nitrogenous bodies that could be extracted. The experiments, the results of which are contained in Table I, have fully confirmed this supposition. Before presenting the results, however, we shall briefly describe the manner in which the peat was extracted with the various reagents. A definite amount of peat was transferred to a flask, then sulphuric or hydrochloric acid previously diluted with distilled water was added. The contents of the flask were shaken to a uniform mass, heated to the boiling point and kept boiling under a reflux condenser for a certain number of hours. Or, instead of boiling with reflux condenser, the flask containing the peat with the reagents was put into an autoclave where it was kept under a constant pressure. The boiled mass was then filtered and washed with boiling water. The peat remaining on the filter was then transferred to a flask, distilled water added, boiled for a few minutes, sucked off, washed with hot water, and these operations repeated another time. Filtrate and washings were evaporated and filled up to a definite volume, usually to 500 or 1000 cc., of which 100 or 200 cc. were taken for nitrogen determinations by the Kjeldahl method. The nitrogen found was calculated to the original volume. Results of this experiment will be found in Table I, under method (*a*).

---

[1] All of the peat samples referred to in this paper were very kindly furnished by Dr. Chas. A. Davis, of the United States Geological Survey.

Since the repeated boiling and washing with hot water, as well as the filtrations, require considerable time, this method was modified in a number of cases as follows: After digestion of the peat for a specified length of time, either under reflux condenser or in the autoclave, the flask content was cooled to room temperature and filled up to a definite volume with distilled water. After shaking, it was filtered through a dry filter, and two portions of the filtrate were taken for nitrogen estimations by Kjeldahl's method. The nitrogen thus found was calculated to the volume of the liquid minus the volume occupied by the peat. The results of this experiment will be found in Table I, under method (*b*). That these two methods differ to a degree in their results may be partly due to the high absorptive power of peat for ammonia and other nitrogenous substances.

In glancing at the table, one can see at once that the concentration of the acid and the duration of digestion have the greatest influence, whereas the quantity of the reagents used has only a slight influence upon the percentage of nitrogenous bodies that can be extracted from the peat. Thus, comparing the experiments 1 and 2, 4 and 8, 6 and 7, where, with the exception of the time of digestion, all the conditions were the same, we find that the percentage of nitrogenous substances extracted rises with increased hours of digestion. Also we notice, by comparing experiments 3 and 4, having equal hours of digestion, that, although the amount of acid used in the latter is considerably smaller than in 3, yet the percentage of extracted nitrogen is about 12 per cent. higher, showing the predominant influence of the concentration of the sulphuric acid. The same

TABLE I.—QUANTITY OF NITROGEN EXTRACTED FROM PEAT UNDER VARIOUS CONDITIONS.

		Reagent used.						Nitrogen extracted.			
									Method (*a*).		
No. of exp.	Grams of oven-dried peat.	H_2SO_4, grams	H_2O, grams.	Strength of acid (per cent. by wt.).	Ratio of weight of reagent to weight of oven-dried peat.	Hours digested.	Method of digestion.	Method (*b*). Per cent. of total N in peat.	Gram.	Per cent. of total N in peat.	Per cent. of oven-dried peat.
1	4.7415	60.8	118.0	33.3	38	28	Boiling under reflux condenser,	50 47	0.06605	50.84	1.39
2	4.7415	60.8	118.0	33.3	38	10	Boiling under reflux condenser,	43.09	0.05616	43.23	1.19
3	4.7415	85.5	337.0	20.0	90	28	Boiling under reflux condenser,	39.22	0.06171	47.50	1.30
4	4.7415	142.5	150.0	47.5	63	28	Boiling under reflux condenser,	55.41	0.07750	59.65	1.63
5	4.7415	121.6	236.0	33 3	77	25	Treated in autoclave, 7/8 atm. pressure,	51.12	....	...	....
6	9.4830	128.3	250.0	33.3	41	32	Boiling under reflux condenser,	...	0.14545	55.98	1.53
7	9.4830	128.3	250.0	33.3	41	35	Boiling under reflux condenser,	...	0.14690	56.54	1.55
8	9.4830	285.0	300.0	47.5	63	30	Boiling under reflux condenser,	...	0.16090	61 92	1.70
9	28.449	286.9	300.0	47.5	21	72	Boiling under reflux condenser,	...	0.49842	63 94	1.75
10	28.449	...	300.0	....	11	16	Boiling under reflux condenser,	3.73	.....	...	....
11	28.449	..	500.0	....	18	10	Treated in autoclave, 7/8 atm. pressure,	5.77	.....	...	....
12	28.002[1]	199.5	388.0	33.3	21	60	Boiling under reflux condenser,	...	0.34601	58.56	1.24
13	28.002[2]	199.5 HCl	388.0	33.3	21	60	Boiling under reflux condenser,	...	0.35928	60.81	1.28
14	9.4830	136.2	222.3	38.0	38	30	Boiling under reflux condenser,	...	0.14549	55 99	1.53

[1] For this experiment a black peat was used which passed through a 20-mesh sieve.

[2] Black peat passing through an 80-mesh sieve.

conclusion can be drawn from experiments 1 and 3. What is true of the sulphuric acid is also true of the hydrochloric acid, which extracts about the same percentage of nitrogen as does the sulphuric acid under the same conditions. Thus experiments 4, 8 and 14, with the same or about the same hours of digestion, show that the 47 per cent. sulphuric acid extracted more nitrogen than the 38 per cent. hydrochloric acid, whereas from experiments 1 and 14 it follows that the hydrochloric acid of a higher concentration was able to extract more nitrogen than the sulphuric acid of a lower concentration.

The experiments 10 and 11 show how small an amount of nitrogenous bodies can be extracted from the brown peat by means of water. This also holds true for other types of peat, for instance, for black peat as well as for weathered brown peat.

That from a peat in a finer state of division more nitrogen can be extracted than from a coarser peat is plainly seen from experiments 12 and 13, conducted under exactly the same conditions with the exception of the fineness to which the respective peat samples were reduced. From this it follows further that the percentages of nitrogen extracted from the brown peat and given in Table I should be considered as minimum figures, since all the experiments, with the exception of 13, were made with peat which passed a 20-mesh sieve.

TABLE II.—NITROGEN EXTRACTED BY REPEATED DIGESTION WITH ACID.

No. of experiment	Digestion.	Amount of oven-dried peat. Grams.	Strength of H_2SO_4 (per cent by weight).	Hours digested.	Nitrogen extracted. Grams.	Nitrogen extracted. Per cent. of total nitrogen	Nitrogen extracted. Per cent. of oven-dried peat.
1	1st	4.7415	33.3	10	0.05616	43.23	1.19
1	2nd		33.3	11	0.01300	10.01	0.27
1	3rd		33.3	29	0.01248	9.61	0.26
1	4th		33.3	32	0.00710	5.47	0.15
					Total,	68.32	1.87
2	1st	7.5864	25.4	10	0.09507	45.74	1.25
2	2nd		33.3	15	0.01803	8.67	0.24
2	3rd		25.0	22	0.01184	5.70	0.16
					Total,	60.11	1.65
3	1st	4.7415	33.3	28	0.06605	50.84	1.39
3	2nd		33.3	29	0.01360	10.47	0.29
3	3rd		29.1	42	0.00842	6.48	0.18
					Total,	67.79	1.86
4	1st	9.4830	33.3	32	0.14545	55.98	1.53
4	2nd		33.3	49	0.01155	4.45	0.12
					Total,	60.43	1.65

But, on the other hand, even boiling for several days with quite strong acid did not dissolve out all the nitrogen contained in the peat. Since the separation of different organic, nitrogenous bodies into groups can be accomplished only in an acid solution, the question as to whether it is possible to extract all the nitrogen from peat by means of acids was of considerable importance. To definitely decide this question, a few peat samples were boiled for a number of hours with fairly strong acid, filtered and thoroughly washed with hot water. The peat was re-extracted several times, being thoroughly washed with hot water after each extraction. The filtrates and washings, after each digestion, were filled up to a definite volume and the nitrogen estimated according to Kjeldahl's method. Table II contains the results obtained through repeated digestions.

In reviewing the results of Table II, we can readily see that the total amount of nitrogen extractable from peat can be increased a few per cent. by repeated digestion, although even in the latter case it was not possible to obtain all the nitrogen in solution, 68.32 being the highest percentage of nitrogen extracted with acid. However, taking into consideration experiments 12 and 13, of Table I, as well as experiment 1 of Table II, we are justified in saying that at least 70 per cent. of the nitrogen can be obtained in solution if the digestion with acid is performed with a brown peat that has passed through an 80-mesh sieve. But the question as to whether it is possible to extract all the nitrogenous bodies from peat by digesting with acid must be answered in the negative, at least this is true under the conditions given in Tables I and II.

Separation of the Organic Nitrogenous Bodies into Different Groups.

As already mentioned, practically all the nitrogen contained in the brown peat is of organic nature. The quite small amount of ammonia present as such in the peat is, it should be remembered, also represented in the total amount of ammonia obtained by distilling the acid-treated peat with magnesium oxide. Hence, we must subtract the ammonia present as such in the fresh peat from this total amount of ammonia in order to find the ammonia corresponding to the amides only. Table III shows the percentage of the different nitrogenous groups contained in the brown peat.

From Table III it can readily be seen that the strong acid (47.5 per cent.) gave about six per cent. more nitrogen in solution than the weaker acid, and that this nitrogen was chiefly amido nitrogen, and monamino nitrogen. When we consider the nitrogen in solution as 100 and reduce to this basis the data in Table III, we get the figures contained in Table IV.

The percentage of monamino nitrogen given in this table was found by difference from one hundred. This percentage was usually higher

TABLE III.—AMOUNT AND PERCENTAGE OF NITROGEN CONTAINED IN THE DIFFERENT GROUPS IN BROWN PEAT.

No of expt.	Oven-dried peat. Grams.	Total nitrogen in peat Gram.	Strength of H_2SO_4. Per cent. by weight.	Nitrogen extracted. Gram	Nitrogen extracted. Per cent of total nitrogen in peat.	Nitrogen extracted. Per cent. of oven dried peat.	Ammoniacal nitrogen originally contained in peat. Gram.	Ammoniacal nitrogen originally contained in peat. Per cent of total nitrogen in peat.	Ammoniacal nitrogen originally contained in peat. Per cent of oven-dried peat.
1	9.483	0.25983	33.3	0.14545	55.98	1.53	0.00417	1.60	0.044
2	9.483	0.25983	33.3	0.1469	56.54	1.55	0.00360	1.39	0.038
3	9.483	0 25983	47.5	0.16020	61.65	1 69	0.00360	1.39	0.038
4	28.449	0 77950	47.5	0.49842	63.94	1.75	0.01252	1.61	0.044
Av.,	....	......	....	.....	59.53	1.63	.....	1.50	0.041

No. of expt.	Amido nitrogen. Gram.	Amido nitrogen. Per cent of total nitrogen in peat.	Amido nitrogen. Per cent. of oven-dried peat.	Diamino nitrogen. Gram.	Diamino nitrogen. Per cent. of total nitrogen in peat.	Diamino nitrogen. Per cent. of oven-dried peat	Monamino nitrogen. Gram.	Monamino nitrogen. Per cent. of total nitrogen in peat.	Monamino nitrogen. Per cent of oven-dried peat.
1	0.03570	13.74	0 376	0.00814	3 13	0.086	0.09744	37 51	1.03
2	0.03627	13.95	0.382	0.00828	3.19	0 087	0.09875	38 01	1.04
3	0.04694	18 06	0 495	0 00543	2.09	0 057	0.10423	40.11	1.10
4	0.14278	18 32	0.502	0.02681	3.44	0 094	0 31631	40.57	1.11
Av.,	.....	16.02	0.439	.....	2.96	0.081	.....	39.05	1.07

than the one directly found by Kjeldahlizing the filtrate from the phosphotungstic acid precipitate. For instance, in experiment 2 the percentage of monamino nitrogen directly found was only 62.83 and in experiment 3 it was 64.25 per cent. instead of 67 22 and 65.06, respectively. The chief reason why the direct determination usually gives too low a percentage of the monamino acids lies in the difficulty of a complete oxidation of the nitrogenous bodies in the presence of an excess of phosphotungstic acid.

TABLE IV.

Number of experiment.	Per cent. of nitrogen in solution as Ammoniacal nitrogen originally contained in peat.	Per cent. of nitrogen in solution as Amido nitrogen.	Per cent. of nitrogen in solution as Diamino nitrogen.	Per cent. of nitrogen in solution as Monamino nitrogen.	Total nitrogen in solution.
1	2.87	24.54	5.59	67.00	100
2	2.45	24.69	5.64	67.22	100
3	2.24	29.31	3.39	65.06	100
4	2.51	28.65	5.38	63.46	100
Average,	2.52	26.80	5.00	65.68	100

An attempt was made to isolate in substance and, if possible, to identify the diamino and monamino acids present in the peat. For this purpose a brown peat from Chelsea, Michigan, was used, of the same type as the one previously described. Its analysis, calculated to peat free of water and ash, gave: C, 60.03; H, 5.73; N, 2.38.

With this brown peat the following experiments were made:

To 54.94 grams of air-dried peat corresponding to 50 grams of oven-dried peat, a mixture of 150 grams concentrated sulphuric acid and 300 grams of water was added, then heated to the boiling point, and kept boiling under reflux condenser for 14 hours. During the boiling, development of hydrogen sulphide was noticed. (Hydrogen sulphide was detected when another sample of peat was digested with hydrochloric acid.) The flask content was filtered, the peat remaining on the filter was transferred to a flask, boiled with water, filtered and washed with hot water. These operations were repeated three times. Filtrate and washings were evaporated, filled up to 1000 cc., and two Kjeldahl determinations made to determine the amount of extractable nitrogenous bodies. The peat extract was then treated with a hot solution of barium hydroxide in order to remove nearly all the sulphuric acid. The barium sulphate was filtered out, boiled with water three times, and each time sucked off and thoroughly washed. Filtrate and washings were somewhat concentrated and then treated with magnesium oxide on a water bath until all ammonia was removed. Barium hydroxide solution was then added in excess; the precipitate, consisting chiefly of magnesium hydroxide and barium sulphate, was filtered out and then extracted three times with hot water. Filtrate and washings were then united and sulphuric acid added in some excess to remove the baryta. The filtrate containing the organic nitrogenous bodies was treated according to the method given by A. Kossel for the separation and identification of histidine and arginine as silver compounds. The result was a negative one.

The resulting filtrate from the above procedure was acidulated with sulphuric acid and treated with hydrogen sulphide. The new precipitate consisting of barium sulphate and silver sulphide was filtered out, extracted with hot water, the filtrate and washings were somewhat concentrated and sulphuric acid was added so as to make the solution contain five per cent. It was then treated with phosphotungstic acid. A precipitate was obtained which was washed with a five per cent. sulphuric acid and then treated with barium hydroxide to remove the phosphotungstic acid. The filtrate was freed from barium by means of carbon dioxide, evaporated nearly to dryness, taken up with hot water and filtered. The filtrate, when evaporated nearly to dryness, consisted of a few drops of a brown sirup. This, treated with picric acid, gave a yellow precipitate too small in quantity for identification.

The filtrate from phosphotungstic acid precipitate, supposed to contain monamino acids, was treated with barium hydroxide to remove the phosphotungstic acid and then treated with carbon dioxide to remove the excess of barium hydroxide. The filtrate from barium carbonate showed the Millon reaction. It was natural enough to think of tyrosine. On the other hand, it must be taken into consideration that nearly all benzene derivatives in which one hydrogen atom is replaced by the hydroxyl group give the same reaction. Considering the relation of peat to protein decomposition products, phenol, ortho- or paracresol or tyrosine were possible.

On adding iron chloride to the filtrate from barium carbonate, no violet or blue color reaction was noticed. Addition of bromine water did not cause any precipitate. These two negative reactions showed that the filtrate under consideration did not contain either phenol or cresol. The non-volatility of the substance in question spoke in favor of tyrosine; however, identification of the tyrosine by means of the microscope or Piria's test could not be accomplished, since the tyrosine was not obtained in substance. This will be comprehended when we state that altogether only 0.43 gram nitrogen was originally in the shape of organic compounds, of which a part was lost through a number of operations mentioned above, and that the remaining nitrogen was very likely present in the shape of various monamino acids.

Weathered Brown Peat.

It was of interest to learn whether the peat undergoes changes, and if so of what nature, when subjected to atmospheric influences. For this purpose a sample of brown peat was taken which had been weathering for two or three years on the surface of the bog. The analysis of this peat reduced to the water-free basis, gave: C, 54.35; H, 5.56; N, 2.69; S, 0.34; ash, 3.79; oxygen (by difference), 33.27.

The nitrogen of the peat was separated into the different groups. The results are given in the table below:

TABLE V.—AMOUNT AND PERCENTAGE OF NITROGEN CONTAINED IN THE DIFFERENT GROUPS IN WEATHERED BROWN PEAT.

				Nitrogen extracted.			Ammoniacal nitrogen originally contained in peat.		
No. of expt.	Oven-dried peat.	Total nitrogen in peat.	Strength of acid. Per cent. by weight.	Gram.	Per cent. of total nitrogen in peat.	Per cent of oven-dried peat.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.
			H_2SO_4						
1	9.596	0 25813	33.3	0.15735	60.96	1.64	0 00048	0.186	0.005
			HCl						
2	9.596	0.25813	38.0	0.17394	67.38	1.81	0.00048	0.186	0.005
Av.,					64.17	1.72		0.186	0.005

TABLE V (*Continued*).

No. of expt.	Amido nitrogen.			Diamino nitrogen.			Monamino nitrogen.		
	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.	Gram.	Per cent. of total nitrogen in peat.	Per cent. of oven-dried peat.
1	0.03773	14.62	0.393	0.0	0.0	0.0	0.11914	46.15	1.24
2	0.04058	15.72	0.423	0.0	0.0	0.0	0.13288	51.48	1.38
Av.,	....	15.17	0.408	...	0.0	0.0	....	48.81	1.31

By calculating the data in Table V to the nitrogen in solution as a basis, we get the following table:

TABLE VI.

Number of experiment.	Nitrogen in solution as				Total nitrogen in solution.
	Ammoniacal nitrogen originally contained in peat.	Amido nitrogen.	Diamino nitrogen.	Monamino nitrogen.	
1	0.30	23.99	0.0	75.71	100
2	0.28	23.33	0.0	76.39	100
Average,	0.29	23.66	0 0	76.05	100

When we compare Tables V and VI with Tables III and IV, we can readily see that certain changes took place in the nitrogenous groups by virtue of the agencies active in the weathering process. In the first place we notice that whereas in the brown peat, prior to the weathering process, the percentage of ammoniacal and amido nitrogen was 0.041 and 0.439, it changed to 0.005 and 0.408, respectively, in the weathered peat. Thus, through the weathering, a total decrease of 0.067 per cent. of ammoniacal and amido nitrogen took place, through leaching or some other cause. This may account for the fact that while the brown peat had 2.52 per cent. of ammoniacal and 26.80 per cent. of amido nitrogen, the weathered brown peat had 0.29 per cent. and 23.66 per cent., respectively, calculated to the nitrogen in solution as basis. This, as well as the disappearance of the diamino nitrogen in the weathered peat, must have necessarily increased the percentage of monamino acids in the weathered peat. It should, however, be borne in mind that, while the estimations of ammoniacal and amido nitrogen give accurate results, the determination of diamino nitrogen is not quite satisfactory. This influences, of course, the monamino nitrogen, since the latter is calculated by difference.

Considering the changes in the weathered peat, the assumption was justified that the solubility of the nitrogenous substances in the peat must have changed. From Table I it was evident that the solubility in water of the nitrogenous bodies contained in the brown peat is very small. It was of interest to learn the solubility in water of the weathered brown peat. For this purpose a few grams of peat were transferred to a flask, a definite amount of water added, mixed, digested, then filled up usually to 500 cc., mixed, filtered, through a dry filter, and two portions of 200 cc. each taken for Kjeldahlization. The nitrogen thus found was recalculated to the total volume. Table VII shows the results of these experiments:

TABLE VII.—THE SOLUBILITY IN WATER OF THE NITROGENOUS BODIES IN WEATHERED BROWN PEAT.

Number of experiment.	Oven-dried peat. Grams	Distilled water. Grams.	Hours digested.	Method of digestion.	Nitrogen extracted. Gram.	Per cent. of total nitrogen in peat.	Per cent of oven-dried peat.
1	4.798	400.0	10	Autoclave at $^3/_4$ to $^7/_8$ atm. pressure,	0.01172	9.08	0.25
2	2.8788	300.0	16	Boiling under reflux condenser,	0.00685	8.85	0.24
3	4.798	500.0	60	Shaken 10 minutes each hour, room temperature,	0.00300	2.32	0.06

From these experiments it follows that the solubility in water of the nitrogenous compounds in the weathered brown peat increases with the rise of temperature. This was also the case with the brown peat as dug from the bog, as can be seen from experiments 10 and 11, in Table I, and holds true also for the black peat. In other words, the solubility in water of the nitrogenous compounds in the various types of Michigan peat is in certain limits a function of the temperature. This being the case, we can further assume that the peats digested at higher temperature and pressure in a suitable autoclave will give a larger amount of water-soluble compounds than was obtained, for instance, in experiment 1, Table VII. That digestion at a higher temperature gives a higher percentage of water-soluble nitrogenous compounds is very likely due, in part, to hydrolysis of the nitrogenous bodies present in the peat.

By comparing Tables IV and VI it is readily seen that only about ten per cent. of the nitrogen in acid solution (and still less of the total nitrogen in the peat) has changed during weathering during two or three years, and that, in addition, the changes of the nitrogenous bodies did not go far enough to be converted, for instance, into ammoniacal nitrogen.

Conclusions.

While the data in hand do not warrant conclusive deductions as to the agricultural value of peat soils, for which further investigation will be necessary, the results obtained and given in this paper permit of drawing the following conclusions:

1. There are no nitrates in the types of Michigan peat soil examined.

2. The amount of ammonia is small, ranging from a few thousandths to a few hundredths of one per cent., this representing the nitrogen available immediately as plant food. In the case of the brown peat, the amount of ammonia is sufficient to meet the needs of one or two crops, as is evident from the following: There are in an acre-foot in round numbers 170 tons of oven-dried peat, with 0.041 per cent. ammoniacal nitrogen, making 0.0697 ton or 139.4 pounds nitrogen as ammonia.

3. Practically all the nitrogen in the peat is of organic nature.

4. The bulk of the organic nitrogen, namely from two-thirds to three-quarters calculated upon the nitrogen in solution, by boiling with acids, is present in the form of monamino acids, about one-quarter in the form of amides and the rest of the nitrogen represents diamino acids.

5. Through weathering, the organic nitrogenous bodies present in the brown peat change quite slowly.

REVIEW.

SOME RECENT ADVANCES IN ORGANIC CHEMISTRY.

Jan. 1, 1908–July 1, 1909.

BY L. H. CONE.

Received December 13, 1909.

Among the advances in organic chemistry during the last few years which have been remarkable for the difficulty of the experimental work involved are those which have been made at the border line between pure organic and physiological or biochemistry. These have deservedly attracted very wide attention.

Proteins.—Naturally one thinks first of Fischer's already classic work on the proteins when biochemistry is brought under discussion. This work has been steadily continued and polypeptides have been prepared of every naturally occurring amino acid, with the exception of five, which are very difficult to obtain or for which special methods will have to be worked out. The number of polypeptides isolated from the partial hydrolysis of proteins has constantly increased and five of these so isolated have been found to be entirely identical with those previously prepared synthetically in the laboratory.[1] Thus Fischer's theory of the protein constitution has been steadily strengthened. A discussion of the impetus which this theory has given to the more scientific study of problems of digestion, of assimilation, and of ferment action, lies without the province of this review, but a casual glance at the physiological literature will show the valuable service which the theory is rendering.

Early in the study of the polypeptides it became apparent that in order to obtain any large number of derivatives of the hydroxyamino acids some method would have to be devised for the temporary protection of the hydroxyl group so that hydroxyamino acid chlorides could be prepared. Fischer[1] has solved the problem by shaking the hydroxy acid to be protected, in alkaline solution with chlorocarbonic methyl ester, when the carbomethoxy group is introduced.

---

[1] "Abderhalden-Physiologische Chemie," 2nd Edition, p. 258 (1908).

$$HOC_6H_4CH_2.CH.NHR.COOH + CH_3OCOCl = CH_3OCO.OC_6H_4CH_2.CH.NHRCOOH + HCl.$$

The derivative thus obtained can be readily changed into the acid chloride by the action of phosphorus pentachloride and the acid chloride can be used for condensations. In the condensed product the hydroxyl group can easily be regenerated by hydrolysis with alkali. By means of this reaction a tetrapeptide, hitherto unattainable, containing tyrosine, has been prepared. The method has, however, a wider application in the synthesis of aromatic hydroxyketones, of which Fischer has prepared a number hitherto obtainable only with difficulty. He has carried the reaction still further and has prepared a number of gallic acid derivatives, among them a crystalline compound which was probably digallic acid.[2] This has not as yet been obtained entirely pure, so its relation to tannic acid is still uncertain.

Fischer's studies of the optical properties of the amino acids have also led to valuable results. Together with Raske[3] he treated the ethyl ester of *l*-serine with phosphorus pentachloride and obtained α-amino-β-chloropropionic ethyl ester. On reduction this yielded *d*-alanine. By treating the same chlorine derivative with barium hydrosulphide they obtained *l*-cysteine, which on oxidation gave *l*-cystine. This series of reactions proves that *l*-serine, *d*-alanine and *l*-cystine, the naturally occurring forms of these acids, all have the same configuration. Previously Fischer and Jacobs[4] had shown that *l*-serine gives *l*-glyceric acid with nitrous acid, Neuberg and Silberman[5] had shown that *l*-glyceric acid and *l*-tartaric acid have the same configuration, and Fischer had connected the configuration of *d*-tartaric acid with rhamnose, so that if all steps in the work were correct we have the beginning of a rational classification of the optically active mono-amino acids. Some doubts have been thrown on the correctness of the results of Neuberg and Silbermann however, so that the relationship between the amino acids and glucose is not yet entirely certain.

The results obtained by Fischer and Scheibler[6] in their study of "Walden's reversal" are interesting but too complex to be given here.

Nucleic Acids.—The problem of the constitution of the nucleic acids has been a difficult but attractive field. It has been known for some time that the nucleic acids have three constituents, carbohydrate, phosphoric acid, and purine or pyrimidine bases. The manner and order of linking of these constituents have not been known nor has the carbohydrate constituent been identified beyond question. That the carbohydrate in most nucleic acids is a pentose is now generally agreed, and Levene and Jacobs[7] have very recently shown that in four nucleic acids examined by them the same pentose is present and this pentose is very probably *l*-ribose. Burian, through his studies upon the diazonium compounds of the purine bases, has rendered it very probable that the purine group is bound in the nucleic acid molecule through its imide hydrogen in the position seven.[1] No sharp experimental evidence has, however, been brought to show the order of coupling of the constituents in the molecule till recent papers by Levene and Jacobs.[2] By acid hydrolysis they obtained a phosphoric acid-pentose complex which had strong reducing power and in which therefore the aldehyde group of the pentose was free. By neutral hydrolysis of the barium salts of several nucleic acids they then obtained a purine base-pentose complex which had no reducing power. From these facts they conclude that the pentose must be coupled ester-like through one of its hydroxyls to the phosphoric acid and glucoside-like through the aldehyde group to the purine base. Guanylic acid would be then as follows:

---

[1] *Ber.*, 41, 2860 (1908).

[2] *Ibid.*, 41, 2875 (1908).

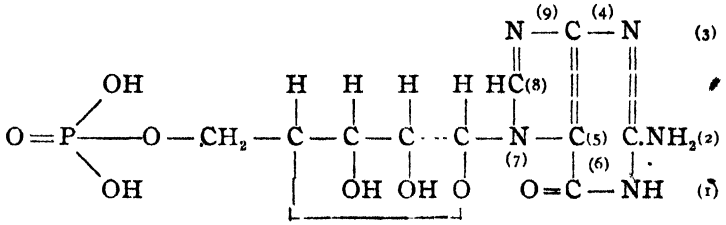
[3] *Ibid.*, 40, 3717 (1907); 41, 893 (1908).

[4] *Ibid.*, 40, 1057 (1907).

[5] *Z. physiol Chem.*, 44, 134 (1905).

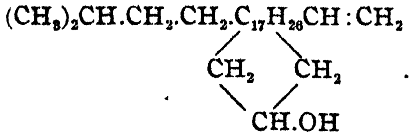
[6] *Ber.*, 41, 889, 2891 (1908).

[7] *Ibid.*, 41, 2703 (1908); 42, 335, 1198, 2102, 2469 and 2474 (1909).



Such a complex they call a "mono-nucleotide" and suggest that the nucleic acids are made up of several of these complexes all alike or different as the case may be, linked together through the phosphoric acid, just as the proteins are composed of polypeptides bound together and the polysaccharides of mono-saccharides coupled in chains of varying length.

Cholesterol.—Through the painstaking work of Windaus[3] a great deal has been added to our knowledge of the constitution of cholesterol. By the judicious application of different oxidizing agents in rotation he has been able to break off various side chains till finally an acid, very resistant to oxidation, has been obtained with the compact formula $C_{17}H_{26}(COOH)_4$. The various steps in the oxidation process are too numerous to be given here, but from the results Windaus concludes that he is justified in writing cholesterol, which has the empirical formula $C_{27}H_{46}O$, as



From the structure given it is apparent that of the twenty-seven atoms of carbon in the molecule the functions of ten have been determined.

Chlorophyll.—Although the work of Willstätter[4] and his co-laborers on chlorophyll began to appear several years ago, it has continued into the time supposed to be covered by this review. The conclusions which they have reached may be summarized very briefly. Chlorophyll occurs in at least two different forms, amorphous and crystalline. The amorphous chlorophylls, which apparently predominate in most plants, are all esters of the same high molecular weight unsaturated alcohol, phytol, $C_{20}H_{40}O$, with different complex acids. The crystalline varieties, if they are esters at all, contain only low molecular weight alcohols so soluble in water that they have escaped detection. Both varieties of chlorophyll contain magnesium in the acid part of their molecules, so combined as to be very resistant to alkalies. This magnesium is readily split off by dilute acids and the organic residues remaining may be broken up by severe treatment with strong acids and alkalies into less complex products, a number of which have been isolated and analyzed. Willstätter's results have generally been accepted. Stoklasa[1] has, however, recently published a series of analyses of samples of chlorophyll prepared by himself, in all of which he found very appreciable quantities of phosphorus. The phosphorus is bound in such a labile manner, according to him, that Willstätter removed it by his process of purification. The majority of chemists will probably accept Willstätter's conclusions, however, that the phosphorus is an adhering impurity properly removed during purification.

---

[1] Cf. "Abderhalden-Physiologische Chemie," 2nd Edition, p. 385. *Ber.*, 37, 696, 708 (1904).

[2] *Loc. cit.*

[3] *Ber.*, 40, 2637 (1907); 41, 611, 2558 (1908); 42, 3770 (1909).

[4] *Ann.*, 350, 1, 48 (1906); 354, 205; 358, 205, 267 (1908).

Carbohydrates.—A number of articles of interest have appeared dealing with the carbohydrates and their derivatives. Fischer and Raske[2] have applied the methods of König and Knorr[3] for the preparation of glucosides from acetobromoglucose and alcohols. The essential point of this method is that the alcohol and the acetobromoglucose are shaken together in a neutral organic solvent in the presence of silver carbonate. The silver binds the hydrobromic acid so that the reaction goes to end in neutral solution. The tetraacetylglucosides were obtained in crystalline form and the acetyl groups removed by hydrolysis with barium hydroxide. By this method glucosides of aliphatic, aromatic, and hydroaromatic alcohols were prepared. The glucosides of menthol and borneol thus obtained are the first terpene glucosides to be described. All of the glucosides prepared were hydrolyzed by emulsin and are therefore probably β-glucosides.

Hudson[4] has pointed out certain relations between the molecular rotations of the various sugars. Evidence indicates that α- and β-glucose are both lactones and differ from each other only sterically. This steric difference must be entirely in the fifth, new asymmetric carbon atom which is produced when the aldehyde group of glucose is hydrated and then dehydrated to form a lactone. If the theory of optical superposition holds[5] the optical effect of the four asymmetric carbon atoms common to both forms must be the same. Let this effect be B. The rotation produced by the fifth asymmetric carbon atom will be the same numerically in both forms but will be different in sign, and can therefore be represented by ±A. One form will thus have a rotation of A + B and the other of —A + B, the sum of which will be 2B and the difference 2A. Other aldoses differ from glucose in the configuration of the four originally asymmetric carbon atoms. In their α- and β- forms the fifth or end asymmetric carbon atoms are identical with those in the two forms of glucose, respectively, *i. e.*, ±A. Their rotations may then be represented by A + B′ and —A + B′, the sum of which is 2B′ and the difference 2A. This means that the α- and β-forms of all aldohexoses should have a common difference 2A. The same reasoning may be applied to other sugars. The theory was tested on a number of sugars whose α- and β-forms are known and found to agree fairly well with the facts. If the principle proves to have general application it will be of value in predicting the rotatory power of forms which have not as yet been isolated and will aid in the rational classification of forms as α- or β-derivatives.

---

[1] *Ber. deutschen bot. Ges.*, 26a, 69 (1908).

[2] *Ber.*, 42, 1465, 1476 (1909).

[3] *Ibid.*, 34, 957 (1901).

[4] This Journal, 31, 66 (1909).

[5] Cf. Rosanoff, *Ibid.*, 25, 525 (1906).

Two years ago Slator[1] showed that lactic acid which is added to a sugar solution undergoing alcoholic fermentation is not affected and can be recovered at the end of the fermentation unchanged. He concluded therefore that lactic acid cannot be an intermediate product in the alcoholic fermentation of sugar. Buchner and Meisenheimer[2] did not accept his conclusions at the time but recently they have repeated his experiments, found them correct, and are inclined to accept his conclusions.[3]

Alkaloids and Terpenes.—The constantly growing volume and complexity of the work on alkaloids and terpenes makes it exceedingly difficult for one not specializing in these fields to choose from among the mass of material those results which stand for real advances.

Leuchs[4] has obtained crystalline acids as the result of the oxidation of strychnine and brucine in acetone solution with potassium permanganate. The acids from the two alkaloids are very similar and each contains four atoms of oxygen more and two atoms of hydrogen less than the alkaloid from which it was produced. From this the conclusion seems justified that a group $\underset{|}{\mathrm{HC}} = \underset{|}{\mathrm{CH}}$ was changed into two carboxyl groups and that a secondary alcohol group was oxidized to a ketone carbonyl. In a later paper Leuchs and Schneider[5] describe crystalline sulphonic acids of both alkaloids which they prepared by treating their solutions in sulphurous acid with manganese dioxide. The reaction apparently proceeds according to the following general equation:

$$O + HO_3SH + H.R = RSO_3H + H_2O,$$

and should therefore yield sulphonic acids of any substance RH, in which H is fairly easily oxidized away. The study of these new derivatives of strychnine and brucine bids fair to aid very materially in throwing light upon their constitutions.[6]

Wollfenstein[7] has described and patented a new method for the preparation of atropine and similar alkaloids from tropine and tropic acid or from tropine and other hydroxy acids as the case may be. Atropine is an ester of tropine and tropic acid, and therefore if tropic acid chloride could be prepared and would react normally with tropine the preparation of atropine would probably be very much more quantitative than by the methods at present in vogue.[1] Tropic acid is α-phenyl-β-hydroxypropionic acid and here, as in the case of Fischer's work with tyrosine, the hydroxyl group led to complications. Wollfenstein therefore prepared acetyl tropic acid, from this the acid chloride, and then condensed the acid chloride with tropine. The acetyl atropine thus obtained hydrolyzes into acetic acid and atropine merely by dissolving in water.

---

[1] *Ber.*, 40, 123 (1907).

[2] *Ibid.*, 41, 1414 (1908).

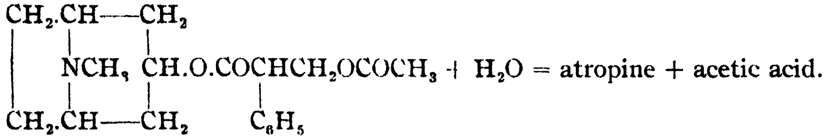
[3] *Chem. Zentr.* 1909, II, 730.

[4] *Ber.*, 41, 1711 (1908).

[5] *Ibid.*, 41, 4393 (1908).

[6] Leuchs und Weber, *Ber.*, 42, 770 (1909).

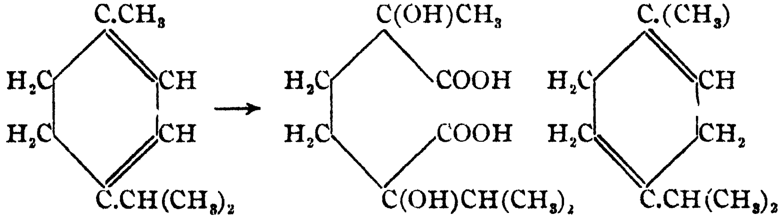
[7] *Ber.*, 41, 723, 733 (1908).



$$\begin{array}{l} CH_2.CH—CH_2 \\ \quad NCH_3 \; CH.O.COCHCH_2OCOCH_3 + H_2O = \text{atropine} + \text{acetic acid.} \\ CH_2.CH—CH_2 \qquad C_6H_5 \end{array}$$

Acetyl atropine.

Wallach[2] has shown that ordinary terpinene is not a homogeneous substance but that it is a mixture of which the main constituent is certainly α-terpinene or $\Delta^{1,3}$-dihydrocymol (I). Samples of terpinene prepared by four different methods, on oxidation all gave an erythrol, $C_{10}H_{16}(OH)_4$, which, on further oxidation yielded α,α′-dihydroxy-α-methyl-α′-isopropyladipic acid (II),



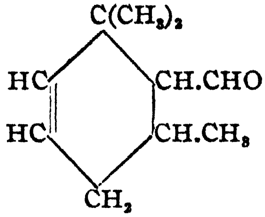
I. II. III.

This acid could come only from α-terpinene (I). Besides the above oxidation products another erythrol was obtained which could not be further oxidized to a substituted adipic acid. This proves that another hydrocarbon is present with α-terpinene in ordinary terpinene, and Wallach concludes that this other hydrocarbon must be γ-terpinene (III). The reasons for this conclusion are too complex to be given here.

A long paper in Liebig's *Annalen* by Merling and Welde[3] on the synthesis of violet perfumes is a valuable contribution to that complex field. Their object was to determine as far as possible the constitutional conditions essential for this especial odor. They first proved that only those aldehydes of cyclo-citral which contain methyl groups in the positions adjacent to the aldehyde group give a compound with the odor of violets on condensation with acetone. This configuration is present in β-irone, the natural oil of violets, which is the condensation product of Δ_4-cyclocitral aldehyde (I) with acetone:

---

[1] *Arch. Pharm.*, 240, 498 (1902).
[2] *Ann.*, 362, 285 (1908).
[3] *Ibid.*, 366, 119 (1909).



I.

They then tested non-cyclic derivatives with the aldehyde group between methyl groups as *e. g.*, isopropyl ethyl acetaldehyde,

$$C_2H_5.CH(CHO).CH(CH_3)_2,$$

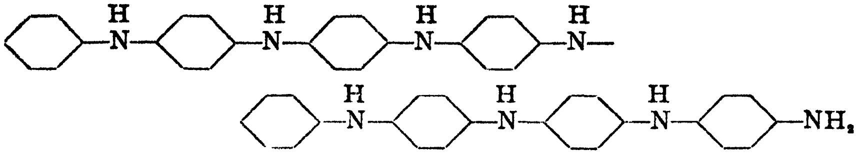
and found that the acetone condensation product of this, while it had a pleasant odor, had no suggestion of violets. The presence of the aldehyde group in a hydroaromatic ring, between methyl groups, seems then to be essential for the production of a violet perfume. The remainder of their paper is taken up with a description of the methods of preparation of the materials for the synthesis of α- and β-irone which are Δ_3- and Δ_4-cyclocitral aldehyde condensation products with acetone, respectively. They conclude that α-irone has no perfume value above that of the natural oil of violets, which is β-irone, and neither have any advantage over the ordinary commercial product which is a mixture of α- and β-ionone, the Δ_2- and Δ_1 derivatives of the same cyclocitral aldehyde condensation product with acetone as the two irones. In passing, it may be worth mentioning that the German patents on ionone expired in April of 1908.

Chemistry of Dyestuffs.—Important advances have been made in the field of the natural dyestuffs so that the constitution of brazilin, haematoxylin, and their derivatives, may be considered as in the main established. Credit is chiefly due to W. H. Perkin, Jr.,[1] and his co-workers for these results, but the work is too complex to permit its being given even in outline in this paper.

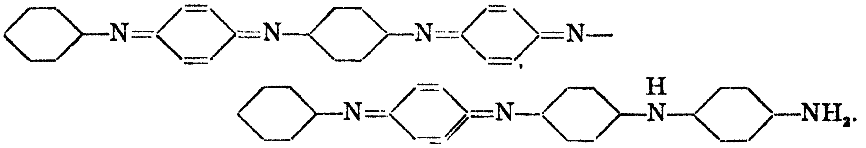
Aniline black in its extreme insolubility and great stability has long defied attempts to gain an insight into its constitution. Willstätter,[2] in his characteristically concise manner, has attacked this problem with co-workers and has apparently been able to solve it. He has shown that the oxidation of aniline to quinone does not take place by way of phenylhydroxylamine as an intermediate product, but that aniline black is certainly produced as one of the steps. The amount of oxygen necessary to form aniline black was found to be 1.25 atoms for every molecule of aniline and the black thus produced had the composition $C_6H_{4.5}N$. The questions remaining to be settled were, how many of these units, $C_6H_{4.5}N$, are there in the molecule of aniline black, and how are they combined with each other? The first question was answered by hydrolyzing samples of the black with sulphuric acid when exactly one-eighth of the total nitrogen was split off as ammonia. Quantitative measurements of the amount of quinone obtained by the oxidation of the aniline black answered the second question. A yield of 93–95 per cent. of quinone was obtained. The only compound which seems to satisfy these facts is that one whose leuco base is the following:

[1] *J. Chem. Soc.*, 93, 489, 1115 (1908).

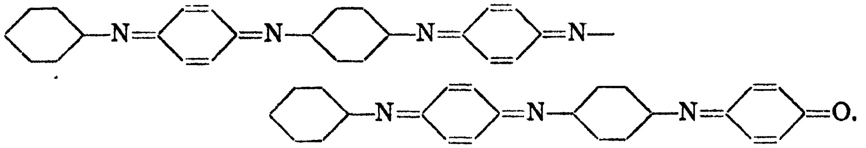
[2] **Willstätter und Dorogi, *Ber.*, 42, 2147, 4118 (1909).**



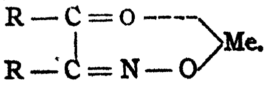
A chain of this type, with continuous para linkings, is the only one which could give a quantitative yield of quinone. The terminal amino group in such a chain is the only one which would be affected by hydrolysis, and therefore if the compound gives up one-eighth of its nitrogen on hydrolysis the molecule must contain eight amino groups, and therefore eight aniline residues in all. The black under discussion would then be $(C_6H_{4\cdot5}N)_8$ or $({}_{48}H_{36}N_8)$, which demands that six hydrogens be oxidized away from the above leuco base to form the dye.



This aniline black is in color blue-black and forms green salts, so it is not the valuable aniline black of commerce. To distinguish it from other blacks Willstätter calls it a triquinoid black. By further regulated oxidation a tetraquinoid black is produced in which the terminal benzene ring substituted with the amino group has become quinoid. This black, whose salts are also green, gives quinone quantitatively on oxidation and also yields one-eighth of its nitrogen on hydrolysis. By this hydrolysis a pure black is produced which does not change color with acids and which seems to be identical with the commercial black. This product must be represented by the following formula:



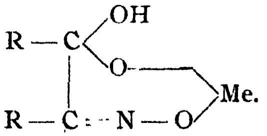
Werner[1] has made use of his theory of inner complex salts in an attempt to explain the nature of the metallic compounds (lakes) formed by mordanting dyes. He assumes the metal in these compounds to be a member of a heterocyclic ring, held there by one principal and by one secondary valence. The differences in color between the true salts of the metals and their lakes are ascribed to the peculiar influence of the secondary valence. The great stability of the lakes and the failure of the metals in them to respond to the ordinary ionic tests are explained on the same basis. The metallic compounds of many simple substances were discussed as illustrations of the theory, as *e. g.*, those of mono-oximes of diketones which he supposes to have the constitution



---

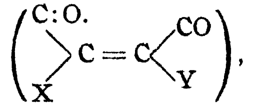
[1] *Ber.*, 41, 1062 (1908).

Liebermann[1] replies to Werner by claiming that the peculiarities of the lakes may all be explained by his old theory of the formation of a heterocyclic ring in which the metal is held by two full valences. Compounds of the type of the above mono-oximes may be explained by assuming that they react in their hydrated form and produce a metallic compound with the structure

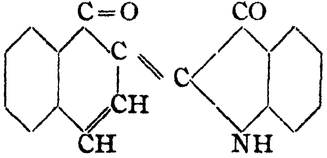


Liebermann's view-point has the advantage of employing only the accepted theory of valence.

Great interest has centered in the last few years in the preparation of dyes suitable for use in the hydrosulphite vat The majority of these dyes are either of the indigo type or derivatives of anthraquinone. The valuable properties of thioindigo have greatly stimulated the preparation of new dyes of the indigo type. Friedlander[2] has coined the word "indigoid" as a class name for all compounds containing the chromophoric complex



in which the ring systems may be either aromatic or aliphatic and in which X and Y may be C, N, S or O. A great variety of compounds of this type can be prepared, of which the compound obtained by the action of isatine chloride on α-naphthol may be cited as an example:



Naphthalin-indole-indigo.

The technically important dyes of this class have been mostly derivatives of thioindigo because the introduction of substituents in the indigo molecule does not very materially alter the color.[3] Some halogenated indigos have been put successfully on the market and Friedländer[4] has shown that the "antique purple" of the classic period was a dibromo indigo obtained from a variety of snail *Murex brandaris* still common in the Mediterranean. Of thioindigo and its halogenated derivatives there are some fifteen different commercial marks for sale, which yield shades from red over orange to the blue and bright blue-violet. A number of these are unsymmetrical derivatives from hydroxythionaphthene and isatin or their derivatives as *e. g.*, thioindigo-scarlet R, which has the following structure:

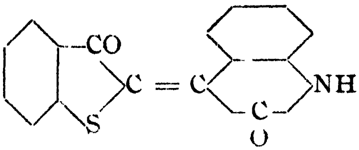
---

[1] *Ber.*, 41, 1430 (1908).

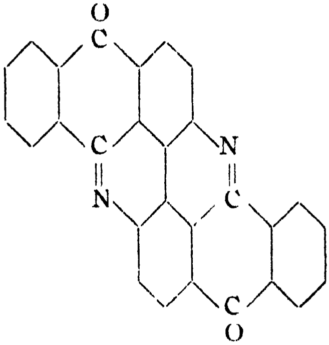
[2] *Ibid.*, 41, 772. *Monatsh.*, 30, 271 (1908).

[3] Cf. J. Rosenberg, *Z. angew. Chemie*, 22, 2129 (1909).

[4] *Ber.*, 42, 765 (1909).



The commercial success of indanthrene and flavanthrene has served to stimulate the production of anthraquinone dyes till at present a very wide range of colors can be obtained with these products. The chemistry of flavanthrene has been studied by Roland Scholl[1] who, in 1907, prepared the compound synthetically, showing it to have the following constitution:



In continuing his work Scholl has obtained seven reduction products of flavanthrene, finally preparing the oxygen-free base flavanthrine.[2]

Constitution and Color.—The vibratory nature of light makes it seem reasonable to conclude that colored substances, which are so by virtue of their power to absorb certain frequencies of vibrations, must have some sort of vibratory motions within themselves which give to them their selective absorptive power. In its ultimate analysis then the cause of color is vibration within the molecule. Whether or not we know enough of molecular physics to attempt at the present time the statement of theories as to the nature of these vibrations is an open question. A number of English investigators[3] have stated such theories, basing them on the results of their spectroscopic studies. Whether or not these theories will be of value to the science, time only will tell.[4] Their experimental work has, however, been of inestimable value in drawing attention to the necessity of applying spectroscopic methods to the study of the problem of color. Many of their observations have shown interesting analogies or have contributed to the settling of structural questions. Two examples from recent papers by Baly may be cited: 1,4,5,8-tetrahydronaphthalene has the same type of absorption spectrum as *p*-xylene, which serves to emphasize the similarity of their structures.[5]

---

[1] *Ber.*, 40, 1691 (1907).

[2] *Ibid.*, 41, 2304, 2534 (1908).

[3] A review of these theories by W. J. Hale is to be found in *Pop. Science Monthly*, 72, 116 (1908).

[4] Cf. Michael, *Ann.*, 363, 45 (1908).

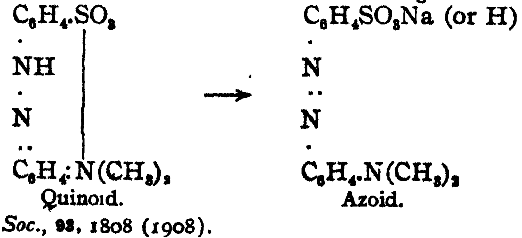
[5] *J. Chem. Soc.*, 93, 1902 (1908).

Cinnamylidenemalonic acid and its esters are yellow but its salts are colorless. The absorption spectra of all three, acid, ester, and salt are alike, thus showing that they are probably all similarly constituted.[1]

Hantzsch[2] has continued to bring forth much evidence in support of his theory that two substances differing in color, though they may be identical in all other properties, must be different in constitution. Hantzsch's theory is in fact a claim for the sufficiency of our present structural hypothesis in explaining color, as far as it can be explained in at all tangible terms. To him every change in color must be accompanied by a change in constitution, and such a change in constitution as can be expressed in terms of the generally accepted methods of structure writing.[3] The extensive debate between Hantzsch and Kaufmann during the past year or so has hinged upon this point. Kaufmann[4] claims that some substances with fixed constitutions will vary their real and their fluorescence color under the influence of mild external agents such as solvents, etc. There must be some variable in the molecule whose changes are casually connected with these variations in color. This variable, non-constitutional part he assumes to be "residual affinities" of the chromophore and the auxochrome groups. The state of these residual affinities, whether in combination with neighboring carbon atoms, with each other, or with molecules of the solvent determines the color of the substance. In terms of this theory all changes of color or of fluorescence can be readily explained, naturally enough, because residual affinities are of such elastic, undefined form that they can readily be molded to suit every demand made upon them. They and their near relatives, partial valences and secondary valences, are in fact the ghosts of modern chemistry. They walk among us constantly so that we all feel their presence, but no one has as yet been able to define their shapes or their sizes or to lay a hand upon them.

Hantzsch's theory, although it fails to explain much, certainly has the advantage of being tangible and of offering many opportunities for the application of experimental tests. A few examples from his work will suffice for illustration. Helianthin in its solid form is violet, in its solutions it is orange, and its sodium salt both in the solid form and solution is orange.[5] The absorption spectra of its orange solutions both as free acid and as salt are identical with similar derivatives whose azo character is not questioned. He concludes, therefore, that the orange forms are all azoid and that the violet form is quinoid as given in the following structures:

Violet. Orange.



$$\begin{array}{l} C_6H_4.SO_3 \\ \cdot \\ NH \\ \cdot \\ N \\ \cdot\cdot \\ C_6H_4{:}N(CH_3)_2 \end{array} \longrightarrow \begin{array}{l} C_6H_4SO_3Na\ (\text{or H}) \\ \cdot \\ N \\ \cdot\cdot \\ N \\ \cdot \\ C_6H_4.N(CH_3)_2 \end{array}$$

Quinoid. Azoid.

---

[1] *J. Chem. Soc.*, 93, 1808 (1908).

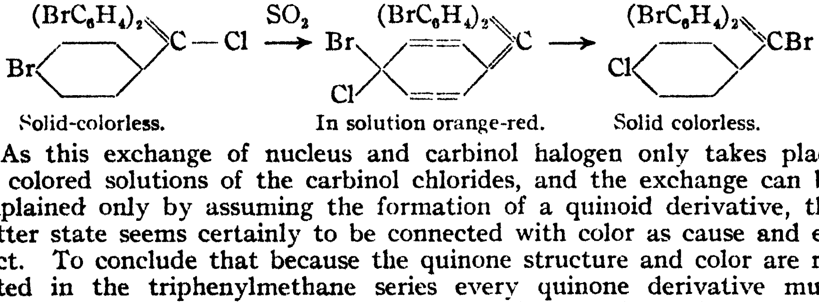
[2] *Ber.*, 41, 1171, 1189, 1204, 1216, (1908); 42, 889, 966, 986, 1000, 1007 (1909).

[3] In his last papers Hantzsch describes certain color changes which he claims are not accompanied by actual structural variations. Attempting to explain these facts he also falls back on secondary valences, whose variations he supposes to cause these more subtle color changes. *Ber.* 42, 985 (1909).

[4] *Ibid.*, 41, 4396, 4413 (1908).

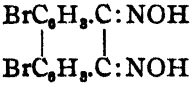
In another paper he describes a large number of salts of oximino ketones, R—CO—CNOH—R, with colorless cations.[1] These salts exist in the greatest variety of colors and mixed shades and he concludes that every salt with a distinctive color must be constitutionally different from salts of other colors and from the colorless form. In the work there is, however, a notable lack of distinctive proof, by reaction or by synthesis, which would positively connect a constitution with a color. The above assumption, for example, that the violet form of helianthin is a quinoid derivative is at best only very probable and it is devoid of actual experimental proof, other than the optical examination of similar derivatives with similar colors.

Gomberg[2] has been able to furnish definite experimental evidence that certain changes from colorless to colored forms in the triphenylmethane series are accompanied by a simultaneous transformation from benzoid to quinoid configurations. *p*-Tribromotriphenylcarbinol chloride, a colorless solid, dissolves in the ordinary organic solvents to a colorless solution but its solution in liquid sulphur dioxide is orange-red. When any of its colorless solutions in organic solvents are evaporated to dryness the original colorless carbinol chloride is recovered unchanged. If, however, the colored solution in liquid sulphur dioxide is evaporated to dryness the result is entirely different. A colorless solid is obtained which is mostly *p*-*p*′-dibromo-*p*″-chlorotriphenylcarbinol bromide. This means that the carbinol chlorine has exchanged places with one of the nucleus bromine atoms. The mechanism of the transformation will be clear if the following equation is examined:



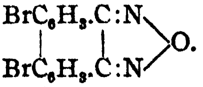
Solid-colorless. In solution orange-red. Solid colorless.

As this exchange of nucleus and carbinol halogen only takes place in colored solutions of the carbinol chlorides, and the exchange can be explained only by assuming the formation of a quinoid derivative, the latter state seems certainly to be connected with color as cause and effect. To conclude that because the quinone structure and color are related in the triphenylmethane series every quinone derivative must always be colored would, however, be stretching the theory further than the facts at present known warrant. A case recently observed by Schmidt and Mezger[3] illustrates this point. 2,7-dibromophenanthraquinone and its dioxime are both colored, but the oxime anhydride which still has the quinone configuration unchanged is colorless:



$$\begin{array}{l} BrC_6H_3.C:NOH \\ \quad | \qquad\ | \\ BrC_6H_3.C:NOH \end{array}$$

Ocher-yellow.



$$\begin{array}{l} BrC_6H_3.C:N\diagdown \\ \quad | \qquad\ | \qquad\quad O. \\ BrC_6H_3.C:N\diagup \end{array}$$

Colorless.

Tautomerism.—Michael[4] has discussed the phenomena of tautomerism and has concluded that two distinct types of reactions are ordinarily classed under this one head. These two classes he distinguishes as (1) desmotropism which is the reversible change of one form into another by the shifting of a hydrogen atom within the molecule and (2) merotropism, which is the irreversible change of one substance into the derivative of another under the influence of an active chemical agent. Both reactions are resultants of two factors, the free energy in the molecule, which naturally tends toward a minimum, and the chemical affinities of the specific groups undergoing change. These ideas Michael has illustrated on numerous examples. With various co-laborers[1] he then investigated several reagents to determine their value as diagnostic agents for stable keto or enol forms. Acetic anhydride, acetyl chloride and phenylisocyanate he found to give unreliable results, but tertiary amines, especially triethyl- and tripropylamine he found gave very consistent results. Tertiary amines unite with enols to form ammonium salts but do not form additive compounds with keto derivatives. The tertiary amines have little power to change keto derivatives over into enols so that only with desmotropes are the results of such a character that they require care in interpretation. A stable keto merotrope will not react with tertiary amines, but a stable enol merotrope will form ammonium salts with considerable evolution of heat, which ammonium salts will yield the free enol again on treatment with acid. A keto desmotrope may be changed over into the enol form, or *vice versa*, under the influence of tertiary amines, according to the stability relations of the two forms. From results with this tertiary amine reaction Michael and Smith classify a number of compounds as stable keto derivatives which have ordinarily been considered to be mixtures of the two forms in equilibrium with each other, *e. g.*, diacetylmethane and acetoacetic ester. This conclusion is not in harmony with the results of numerous physico-chemical investigations, but Michael and Smith point out that these physico-chemical results do not harmonize among themselves and are therefore never to be accepted when they contradict chemical evidence. It is interesting to note in this connection that Auwers[2] has called attention to the fact that physico-chemical methods have been of much less value in clearing up the constitution of the hydroxyazo compounds than have the purely chemical methods.

---

[1] *Ber.*, 42, 966 (1909).

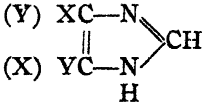
[2] *Ibid.*, 42, 406 (1909).

[3] *Ibid.*, 40, 4560 (1907).

[4] *Ann.*, 363, 20 (1908).

Mannich and Hancu[3] have shown that cyclic ketones, and Hancu[4] has shown that symmetrical aliphatic ketones are tautomeric substances (merotropes according to Michael), in that they yield more or less of the acetyl derivatives of their enol forms on long heating to high temperatures with acetic anhydride. On saponification the acetyl derivatives yield only the original ketones.

Gabriel[5] has shown that where two substituted imidazoles of the form



---

[1] Michael and Smith, *Ann.*, 363, 36, Michael and Cobb, p. 64, Michael and Murphy, p. 94 (1908).

[2] *Ann.*, 360, 11 (1907).

[3] *Ber.*, 41, 564 (1908).

[4] *Ibid.*, 42, 1052 (1909).

[5] *Ibid.*, 41, 1926 (1908).

would be expected only one can be obtained by synthesis. He therefore concludes that this is a case of "virtual tautomerism," where the imide hydrogen atom is in equilibrium between the two nitrogens.

Catalysis.—The mechanism of the catalysis of various organic reactions by acids and bases has been the subject of a number of investigations. Stieglitz[1] and Acree[2] have both obtained experimental evidence in favor of the theory that the catalyzer forms salts with some substance in the reaction undergoing catalysis. Stieglitz investigated the hydrolysis of imino esters and concluded that the rate of hydrolysis of the esters in acid solution is proportional to the concentration of the cation formed by the ester with the acid, and in alkaline solution is proportional to the concentration of the anion formed by the ester with the base. Acree studied the formation of acetooxime from acetone and hydroxylamine and concluded that the catalysis of this reaction by acids and bases depends in both cases upon salt formation with the hydroxylamine. Both investigators agree that the definition of catalysis, as accepted a few years ago, covers only certain ideal cases. Further study is needed before a satisfactory new definition can be formulated. The majority of chemists will probably agree with Stieglitz, Acree and others, that catalyzers exert their influence through the formation of intermediate unstable compounds which probably are salts. Since the work of Collie, Werner, Baeyer, and a host of others on the oxonium theory, the idea that these intermediate compounds are in most cases oxonium salts has steadily gained ground. That they may be carbonium salts has been suggested by Stieglitz,[3] but he concludes that at present the preference must be given to the oxonium form. The author of this review believes, however, that in the end evidence will be found to indicate that these compounds, if salts at all, are really carbonium salts. He bases this view on two things: first, the position of carbon in the periodic system, which would indicate a base-forming power greater than that of either nitrogen or oxygen, and second, on the generally unsatisfactory nature of the evidence in favor of the oxonium theory.

Rosanoff and Prager,[4] and Michael,[5] have simultaneously called attention to the fact that hydrochloric acid, which has always been assumed to be, with a few exceptions, a favorable catalyzer for esterifications, is in a good many cases a negative catalyzer. Michael uses this fact as an argument in support of the theory discussed above, that the catalytic influence of hydrochloric acid upon esterification is due to an intermediate salt formed with the alcohol. Hydrochloric acid will then increase or diminish the rate of esterification according as the acid being esterified reacts more readily with this hydrochloric acid-alcohol complex or with the free alcohol. The chemical nature[6] of the acid undergoing esterification will thus determine whether hydrochloric acid will

[1] *Am. Chem. J.*, 39, 29, 166 (1908).
[2] *Ibid.*, 39, 300 (1908).
[3] *Ibid.*, 39, 48 (1908).
[4] THIS JOURNAL, 30, 1895 (1909).
[5] *Ber.*, 42, 310, 317 (1909).
[6] Cf. Stewart, "Stereochemistry," p. 321.

act as a positive or a negative catalyzer. To determine the real rates of esterification of acids the reaction must be studied in the absence of all catalyzers. V. Meyer based his rule in regard to the esterification of di-*o*-substituted aromatic acids upon results obtained in the presence of hydrochloric acid. Hydrochloric acid acts toward the esterification of these acids as a negative catalyzer, but by heating them with alcohols alone they can be readily esterified. V. Meyer[1] was always very careful to state that his law held only for esterification in the presence of hydrochloric acid, therefore these new facts serve more to broaden his law than to contradict it. Rosanoff and Prager suggest the following wording so as to make the law general: "Aromatic acids, in which one or both of the positions ortho to the carboxyl group are occupied by substituents, unite with alcohols slower but not less completely than acids otherwise constituted."

Willstätter and Mayer[2] have revived a method, already patented and known in the chemical literature, for the reduction of unsaturated compounds with hydrogen at ordinary temperature in the presence of finely divided platinum. From phytol they thus prepared dihydrophytol, oleic acid ester gave stearic acid ester and benzoic acid gave some hexahydrobenzoic acid. Paal[3] has obtained the same results by the use of colloidal palladium.

The use of finely divided nickel oxide for the catalytic reduction of volatile organic substances at high temperatures has become general. Ipat'ev[4] has made several interesting observations on the finer details of this process. Nickel oxide, in an atmosphere of hydrogen, is reduced to metallic nickel at 200°, but when benzene is being reduced to hexahydrobenzene the nickel oxide is heated considerably higher without appreciable production of metallic nickel. If the nickel oxide is heated over the blast before using, its efficiency as a catalyzer is very considerably impaired. By analysis Ipat'ev showed that the unignited nickel oxide held a few per cent. of water and he attributes its better catalytic effect to this moisture. Senderens[5] has shown that silica and aluminium oxide have very peculiar effects upon the decomposition of alcohol and various organic acids at high temperatures. According to the previous history of the silica or the aluminium oxide employed as catalyzer, and the temperature at which the reaction is carried out, alcohol will produce a gas which is pure ethylene, or a mixture of ethylene and hydrogen, or practically all hydrogen. Acetic acid decomposes at 350° in the presence of aluminium oxide into acetone and carbon dioxide.[6] Ethyl ether breaks up at 300° into ethylene and water. If alcohol is passed over aluminium oxide below 300° at, *e. g.*, 240–260°, a good yield of ether is obtained with only slight quantities of ethylene.[7] Sabatier and Mailhe[8] have shown that a mixture of alcohol and ammonia passed over thorium

[1] Cf. *Ber.*, 41, 4695 (1908).

[2] *Ibid.*, 41, 1475 (1908).

[3] Paal und Jerum, *Ibid.*, 41, 2273 (1908).

[4] *Russ. Phys. Chem. Soc.*, 40, 1 (1908).

[5] *Compt. rend.*, 146, 125 (1908).

[6] *Ibid.*, 146, 1211 (1908).

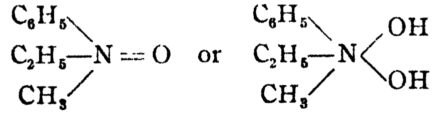
[7] *Ibid.*, 148, 227 (1909).

[8] *Ibid.*, 1[illegible], 898 (1909).

oxide at 360° will form primary ethylamine with some secondary amine and traces of the tertiary amine.

Stereochemistry.—The theory of Guye, that optical activity is a function of the differences between the weights of the groups about the asymmetric carbon atom, has been again brought into discussion. Recent writers[1] on stereochemistry agree that the theory is entirely insufficient, but because it is the only general theory of the relation between constitution and optical activity it still continues to suggest experimental work. Fischer and Flautau,[2] on the suggestion of van't Hoff, prepared propyl isopropyl cyanacetic acid and resolved it into its constituents. The theory of Guy requires that these constituents should be optically non-active, as the propyl and isopropyl group are identical in weight, but they were found to have an activity of ±11.4. Everat and Jones,[3] and Jones and Hill,[4] have examined a number of optically active ammonium derivatives and concluded that the constitutions of the groups about the asymmetric nitrogen have more influence than their weights. Bose and Willers[5] examined 42 optically active substances with seventeen different groups and conclude from their results that the theory of Guye is entirely at variance with the facts. Bose[6] suggests a modified form of Guye's equation for the asymmetry product in which no assumption is made as to the nature of the constants which represent the activity produced by each group about the asymmetric carbon atom. He then shows how such a modified expression suggests experimental tests which will either disprove or will furnish strong evidence in favor of the correctness of Guye's fundamental idea in regard to the asymmetry product. For the mathematical details of Bose's reasoning the original articles must be consulted.

Meisenheimer[7] has been able to prepare an optically active ammonium derivative where two of the five valences of the nitrogen are attached either to oxygen or to two hydroxyl groups:



Ethyl-methyl aniline oxide is optically active in aqueous solution as the free base, or in the form of its salts. As an explanation of this activity he assumes that four valences of the nitrogen atom are directed to the four corners of a tetrahedron and the fifth remains without fixed direction. The space arrangement then becomes similar to that about the asymmetric carbon atom. The two hydroxyls are not alike if the molecule is thus constructed, as one is fixed in position and the other is free to wander, so that the case under consideration would then really belong to the class of optically active ammonium derivatives having five unlike radicles. That the two hydroxyls of the hydrate form in its unionized state are really unlike seems very improbable to the writer of this review.

---

[1] Stewart, "Stereochemistry", p. 101; Werner, "Stereochemie", p. 133.

[2] *Ber.*, 42, 2981 (1909).

[3] *J. Chem. Soc.*, 93, 1789 (1908).

[4] *Ibid.*, 93, 295 (1908).

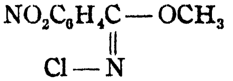
[5] *Z. physik. Chem.*, 65, 702 (1909).

[6] *Physik. Z.*, 9, 860 (1908); *Z. physik. Chem.*, 65, 695 (1909).

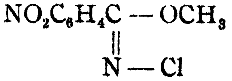
[7] *Ber.*, 41, 3966 (1908).

The phenomenon of auto-racemization so characteristic of the optically active ammonium salts has been investigated by E. Wedekind and his co-workers.[1] They have shown that when the active halogen salts are dissolved in chloroform the iodides racemize the most rapidly, the bromides next, and the chlorides are the most stable. This auto-racemization they proved to be due to the splitting of the ammonium salt into an alkyl halide and a tertiary amine, both of which are non-active.

Stieglitz and Hilpert[2] have isolated two forms of the chloroimido esters of several nitrobenzoic acids. These forms differ distinctly in physical properties, yet all of their reactions indicate that they are structurally identical. They must, therefore, be stereoisomers, probably geometrical isomers, of which one is the syn- and the other the anti-form:



$$\begin{array}{l} NO_2C_6H_4C - OCH_3 \\ \quad\;\;\;\;\;\;\;\;\; \| \\ \;\;\;\;\; Cl - N \end{array}$$



$$\begin{array}{l} NO_2C_6H_4C - OCH_3 \\ \quad\;\;\;\;\;\;\;\;\; \| \\ \quad\;\;\;\;\;\;\;\;\; N - Cl \end{array}$$

This is the first example of geometrical isomerism among derivatives where the nitrogen is attached on one side to a single element.

The limited space allotted for this review makes it impossible to even mention a great many of the valuable results obtained in organic chemistry during the past eighteen months. In view of the recent paper in THIS JOURNAL by W. A. Noyes[3] on "Molecular Rearrangements" that subject, which is at present receiving as much attention as any one field of organic chemistry, has not been discussed. Discussions of the special applications of general reactions, as Grignard's, and Friedel and Crafts' reactions, have been omitted, as well as descriptions of the synthesis of a vast number of new compounds belonging to already well-established classes.

UNIVERSITY OF MICHIGAN, ANN ARBOR.

NEW BOOKS.

Einführung in die allgemeine und anorganische Chemie auf elementare Grundlage. von DR. ALEXANDER SMITH, unter Mitwirkung des Verfassers übersetzt und bearbeitet von DR. ERNST STERN, Assistent am Königl. Material-prüfungsamt zu Gross Lichterfelde-West. Mit einem Vorwort von Dr. FRITZ HABER, ord. Professor an der Technischen Hochschule zu Karlsruhe. G Braun, Karlsruhe, i. B, 1909, pp. 677. Price, M. 9.

American chemists who owe so much of their advanced training to the German universities cannot fail to note with satisfaction that in reforming their methods of elementary chemical instruction the Germans are taking the American curriculum as a model. The German translation of Alexander Smith's laboratory manual which appeared some years ago has been widely adopted, and this excellent translation of the author's larger work may be expected to achieve an equal success. While the treatment of experimental material has remained unaltered, the theoretical portions of the book have been thoroughly revised by the translator with the coöperation of the author. The book is well introduced to German readers in a preface written by the broadest and surest of German teachers and investigators in chemistry.

---

[1] E. and O. Wedekind, *Ber.*, 41, 1029 (1908); E. Wedekind and Paschke, *Ibid.*, 41, 2659 (1908).

[2] *Am. Chem. J.*, 40, 36, 150 (1908).

[3] THIS JOURNAL, 31, 1368 (1909).

In this preface Professor Haber points out the three standpoints from which one may view the great domain of chemical science. The first is based on the comparison of the elements by means of the periodic system, the second on the qualitative representation of substances and reactions through structure formulas, and the third on a quantitative treatment of chemical phenomena according to the fundamental physico-chemical principles. A student who becomes equally familiar with these three methods possesses an immense advantage, comparable with that given by a mastery of several languages acquired in youth. While the use of a single view-point in the teaching of elementary chemistry may be attractive to both teacher and student, yet the more enthusiastically and emphatically the teacher develops this single system, the more difficult the student finds it, when occasion arises, to adopt another point of view. As a result we have physical chemists without the structure-chemical instinct, or organic chemists who lack physico-chemical insight. So misunderstandings arise, and each group seeing only the importance of its own problems forgets that after all there is but one Chemistry, in which the different methods are equally justifiable because equally fruitful. Professor Haber especially commends the book under review for its impartial and thorough treatment of all the general methods of chemistry.

GILBERT N. LEWIS.

General Chemistry for Colleges. By ALEXANDER SMITH, Professor of Chemistry and Director of General and Physical Chemistry in the University of Chicago. New York: The Century Co., 511 pp. Price, $2 15.

The method of treatment employed by the author in his "Introduction to General Inorganic Chemistry" has proved so satisfactory to large numbers of teachers throughout the country that this shorter course in which a similar method and arrangement are employed cannot fail to find a wide field of usefulness. The theoretical chapters differ materially from those of the larger work, and some of the descriptive matter contained in the latter has been omitted. There can be no doubt that the larger text-books of inorganic chemistry which are in common use contain much more information than can be readily assimilated by the average student in his first year of chemical study. It may be questioned whether this is not still true of the shorter course contained in this book.

GILBERT N. LEWIS.

RECENT PUBLICATIONS.

ARMITAGE, F. P.: **A History of Chemistry.** New York: Longmans Green & Co. 8°. 286 pp. $1.60.

AUSTIN, L. S.: **The Metallurgy of Common Metals, Gold, Silver, Iron, Copper, Lead and Zinc.** Second edition. San Francisco: Mining & Scientific Press. $4.00.

BERDEL, EDUARD: **Einfaches chemisches Praktikum für Keramiker, Glastechniker, Metalltechniker usw.** 1 Teil: Chemische Versuche und Präparate. Coburg: Müller & Schmidt.

BOTTOMLEY, S. E.: **Photography in Principle and Practice.** Dawbarn & Ward. 8°, 288 pp., 3 s. 6 d.

CLARK, D.: **Gold Refining.** Pitman: 8°, 124 pp., 12 s. 6 d.

ESCALES, R.: **Die Ammonsalpetersprengstoffe.** Leipzig: Veit & Co. 8 M.

ESCARD, J.: **La fabrication électrochimique de l'acide nitrique et des composés nitrés à l'aide des éléments de l'air.** 2 éd., 8°, 116 s., 4.50 Fr.

EWELL, A. W.: **A Text-Book of Physical Chemistry: Theory and Practice.** Philadelphia: Blakiston's Sons & Co. $2.25.

FAYOL, A.: **Le Caoutchouc.** 8°, 138 s., 7.50 Fr.

FERMUM: **Die Legierungen.** Hannover: Dr. Max Jänecke. 4 M.

FISCHER, E.: **Introduction to the Preparation of Organic Compounds.** Williams & Norgate. 8°, 175 pp., 4 s.

FOWLER, A.: **The Spectrum of Magnesium Hydride.** Dulau: 4°, 2 s. 6 d.

GARRETT, A. E.: **The Periodic Law.** London: Paul, Trench Trübner & Co. 8°, 294 pp., 5 s.

GEMMELL, G. H.: **Chemical Notes and Equations: Inorganic and Organic.** Second edition. Baillière. 8°, 280 pp., 5 s.

GIBBS, W. M.: **Spices and How to Know Them.** Dunkirk, N. Y. W. M. Gibbs. 179 pp. $3.50.

GISSING, F. T.: **Commercial Peat; Its Uses and Possibilities.** C. Griffin: 8°, 202 pp., 6 s.

GOOCH, F. A., AND BROWNING, P. E.: **Outlines of Qualitative Chemical Analysis.** Second edition revised. New York: J. Wiley & Sons. $1.25.

GREGORIUS, R.: **Erdwachs, Paraffin, und Montanwachs, deren Darstellung und Verwendung.** Chemisch-technische Bibliothek Bd. 303. Wien und Leipzig: Hartleben. 286 s., 4 M.

GREINACHER, H.: **Die neueren Strahlen. Radium-Strahlen, Kathoden-, Kanal-, Anoden-, Röntgenstrahlen. In leichtfasslichen Einzeldarstellungen.** Stuttgart: Ferd. Enke. 8°, 130 s., 4 M.

HALE, W. J.: **The Calculations of General Chemistry; with Definitions, Explanations, and Problems.** New York: D. Van Nostrand Co. $1.00.

HARPER, W. B.: **Die Destillation industrielles und forstwirtschaftlicher Holzabfälle.** 2 deutsche aufl. (Bearbeitung von R. Linde). Berlin: J. Springer. 8°, 323 s., 10 M.

HESSE, O.: **Über die Entwickelung der Industrie der aetherischen Öle in den letzten 25 Jahren.** Göttingen: Vandenhoeck & Ruprecht. 8°, 151 s., 4 M.

HOLDE, D.: **Untersuchung der Mineralöle und Fette, sowie der ihnen verwandten Stoffe.** 3 Aufl. Berlin: J. Springer. Geb., 12 M.

HOLLARD, A., U. BERTIAUX, L.: **Analyse des Métaux par Electrolyse. Métaux industriels; alliages, minerals, produits d'usines.** 8°, 256 s., 9.50 Fr.

JAEGER, H.: **Die Bakteriologie des täglichen Lebens.** Hamburg: Leopold Voss. Geb., 8 M.

JAGO, W.: **A Manual of Forensic Chemistry, Dealing Especially with Chemical Evidence, Its Preparation and Adduction.** Stevens. 8°, 264 pp., 5 s.

JÄNECKE, DR. ERNST: **Summary of Alloys. The Employment of Physical Chemistry in Metallography.** Hannover: Dr. Max Jänecke. 3 M.

JENKS, TUDOR: **Chemistry for Young People.** New York: F. A. Stokes Co. 309 pp. $1.50.

JONES, L., AND SCHOOL, F. J.: **The Manufacture of Cane Sugar.** Stanford. 8°, 12 s. 6 d.

KEANE, C. A.: **Modern Organic Chemistry.** London: Walter Scott Pub. Co. 503 pp., 6 s.

KOCH, J.: **Dispersionsmessungen an Gasen im sichtbaren und im ultraroten Spektrum.** Upsala: Akadem. Buchhdlg. 4. 3.50 Kr.

LIESEGANG, R. E.: **Beitrag zur einer Kolloidchemie des Lebens.** I Teil: Theorien: II Teil: Versuche. Dresden: Th. Steinkopff. 8°, geb , 5 M.

LOW, A. H.: **Technical Methods of Ore Analysis.** Fourth edition. New York: John Wiley & Sons. $3.00.

MACKNIGHT, E. F.: **Fertilizer and Acid Plants.** New York: Insurance Press. 8°, 94 pp. $0.50.

MCGREGORY, J. F.: **A Manual of Qualitative Chemical Analysis.** Revised edition. Boston: Ginn & Co. $1.00.

MENGARINI, MARGHERITA TRAUBE, UND SCALA, A.: **Über die chemische Durchlässigkeit lebender Algen- und Protozoenzellen für anorganische Salze und die spezifische Wirkung letzterer.** Berlin: J. Springer. 2 M.

MINDES, J.: **Selbstbereitung pharmazeutischer Spezialitäten.** 2 verm. aufl. Wien: F. Deuticke. 1.50 M.

MORGAN, J. J.: **Blast Furnace Practice.** C. Griffin. 8°, 54 pp., 1 s. 6 d.

MOSER, DR. L.: **Die Bestimmungsmethoden des Wismuts und seine Trennung von den anderen Elementen.** Stuttgart: Ferd Enke. 8°, 126 s. 4 M.

NAGEL, OSKAR: **The Transportation of Gases, Liquids and Solids, by Means of Steam, Compressed Air and Pressure Water.** New York: Oskar Nagel. 200 pp. $2.00.

NEWTH, G. S.: **A Text-Book of Inorganic Chemistry.** New York: Longmans Green & Co. 740 pp. $1.75.

NEWTH, G. S.: **Chemical Lecture Experiments.** New York: Longmans Green & Co. 344 pp. $2.00.

NOELTING, F. A. M.: **Contributions à la connaissance des oxyaldéhydes orthovanilline et l'aldehyde orthovératique.** Mülhausen: Imp. Veuve Bader & Co.

PACZKOWSKI: **Schädliche Nebenwirkungen der Arzneimittel.** 2 Aufl. Leipzig: Edmund Demme. 1 M.

PERKIN, W. H., UND LEAN, B.: **An Introduction to Chemistry and Physics.** Macmillan: 12°, 236 pp., 3 s., 6 d.

ROST, E. F. F., UND HEISE, R.: **Beiträge zur Photographie der Blutspektra**

unter Berücksichtigung der Toxikologie der Ameisensäure. Berlin: J. Springer. 8° 9 M.

RUDOLPH: **Keramik.** Hannover: Dr. Max Jänecke. 2.50 M.

RUER, RUDOLPH: **The Elements of Metallography.** Authorized translation by C. H. Mathewson. New York: John Wiley & Sons. 8°, 342 pp. $3.00.

SCHÄTZLEIN, DR. CHRISTIAN: **Zuckerungstabellen zur gesetzlich erlaubten Verbesserung der Traubensäfte, Traubenmaischen und Weine, sowie der Obst- und Beerensäfte.** Stuttgart: Eugen Ulmer. 1.20 M.

SCHEINER, J.: **Spektralanalytische und photometrische Theorien.** Leipzig: J. A. Barth. 190 s., geb., 6 M.

SCHMIDT, W. A.: **Die Erkennung von Blutflecken und die Unterscheidung von Menschen- und Tierblut in der Gerichtspraxis, zugleich eine Schilderung der Haupteigenschaften des Blutes, sowie der Blutverwandtschaft unter den Tieren.** Leipzig: Quelle & Meyer. 80 Pf.

SCHNEIDER, W.: **Mineralische Düngemittel u. Ernteergebnisse.** Riga: N. Kymmel. 1.80 M.

SCHUBERT, M.: **Die Holzstoff und Holzschliff-Fabrikation.** 2 verm. u. verb. Aufl. von Th. Knösel. Berlin: M. Krayn. 8°, geb., 6.50 M.

SCHUMM, OTTO: **Klinische Spektroskopie.** Jena: Gustav Fischer. 139 s., 6 M.

SELLERS, J. F.: **An Elementary Treatise on Qualitative Chemical Analysis.** Second revised edition. Boston: Ginn & Co. $1.00.

STOCK, A., UND STÄHLER, A.: **Praktikum der quantitativen anorganischen Analyse.** Berlin: J. Springer. Geb., 4 M.

TENNANT, A.: **The American Annual of Photography.** New York: G. Murphy. 328 pp. $1.00. Paper, $0.75.

THORPE, SIR EDW.: **History of Chemistry.** Volume I. Watts: 12°, 148 pp., 1 s.

VANDEVELDE, PROF. A. J. J.: **Elements de chimie génerale; préparatoires à l'études biochimique des fermentations.** Second edition. Paris: Gaudet. 250 s.

WIEN, W.: **Ueber Elektronen.** Vortrag. 2. **Die Fortschritte der iri Wissenschaft berücksicht.** Leipzig: B. G. Teubner. 8°, 39 s., 1.40 M.

WOLF, K.: **Grundzüge der Elektrotechnik zum Gebrauche an gewerblichen Lehranstalten.** Wien: A. Hölder. 8°, 145 s., 1.80 M.

Vol. XXXII. April, 1910. No. 4.

THE JOURNAL

OF THE

American Chemical Society

THE ADIABATIC DETERMINATION OF THE HEATS OF SOLUTION OF METALS IN ACIDS.

[FIRST PAPER.]

By Theodore William Richards and Laurie Lorne Burgess

Received January 21, 1910

Contents.

Introduction, Discussion of Earlier Work, Materials Hydrochloric Acid Zinc, Aluminium, Magnesium, Cadmium, Iron, Apparatus: The Adiabatic Calorimeter, Thermometers, Stirrers, The Platinum Basket, Apparatus for Preventing Loss of Drops, Efficiency of Stirring, Correction for Heat Evolved in Stirring, Possible Errors Caused by Heat Exchange with Surroundings, Correction for Evaporation of Acid, The Heat of Solution of Metals in Concentrated Acids, The Heat of Solution of Zinc; Summary.

Introduction.

The heats of solutions of metals in acids are among the most essential and fundamental of thermochemical data The heats of formation of all the metallic compounds depend upon them, because through them the heat values are referred back to the element. Hence it is highly important for exactness in thermochemistry that these values be determined with great precision.

As a matter of fact, in the past certain difficulties have interfered with the perfection of the measurements. First and foremost among these is the fact that the solution of a metal requires much time, and therefore the always somewhat uncertain correction for cooling in the usual method becomes a serious fraction of the whole rise of temperature. In the second place, the method generally used, namely, the plunging of a weighed sheet of metal into acid, and then withdrawing it, checking the reaction as soon as possible, and determining the amount dissolved by loss in weight, is open to serious criticism. It is impossible that the withdrawal should be so quick as to introduce no error in the results.

The new method of adiabatic calorimetry, recently used at Harvard, seems to be especially suitable for such cases as this, and accordingly, the present investigation concerns itself with the application of this method to the solution of metals in acids This method of calorimetry avoids wholly the cooling correction by surrounding the calorimeter with a jacket, having always precisely the same temperature as the calorimeter itself. The jacket contains an alkali, and as the reaction progresses within the calorimeter, enough acid is added, drop by drop, to this alkali to change its temperature at exactly the same rate as that of the calorimeter proper.

This method overcomes entirely the first fault which exerted an especially detrimental effect upon the early determinations of the heat of solution of metals—this fault being, namely, the large cooling correction, because of the slowness of the process The second difficulty was overcome by another device Instead of dissolving only a part of a large metal sheet or net, we placed the metal in a finely divided condition in a basket, and the reaction was allowed to continue until all which had been placed in the basket was completely dissolved. The calorimetric method allows plenty of time—a slow reaction is as well measured as a quick one. Hence this procedure involves no difficulty, but affords a satisfactory method of overcoming the faults in the doubtful mode of operation previously adopted.

In carrying out experiments by this method, it was found that as the effectiveness increased, another error which also must have affected previous determinations was uncovered In reactions of this kind the solution is not always mixed very thoroughly during the progress of the reaction, and the thermometer does not always fairly represent the average temperature, unless the stirrer is very active. Hence, according to the old method, the cooling correction is not properly calculated, and according to the new method the jacket is not maintained at the right temperature. In either case inaccurate final results will be obtained. Obviously, a correct result is to be hoped for only when the stirring is so active that the temperature is nearly the same throughout the calorimeter. Our experience leads us to believe that early work of this kind did not maintain sufficient equality of temperature. That exceedingly concordant results may be obtained if these precautions are all heeded is shown by the results to be given later.

In brief, this paper presents an account of the highly successful application of the new method of adiabatic calorimetry to one of the most important series among thermochemical data.

Our thanks are due to the Carnegie Institution of Washington, which has granted us generous pecuniary assistance in the prosecution of this work.

Discussion of Earlier Work.

Apparently Thomsen[1] alone, among earlier thermochemists, has measured the heats of solution of most of the metals in acids. We owe much to this eminent investigator, but it is not surprising that his pioneer work, carried out at a time when chemistry was a far less precisely quantitative science than at present, should not have attained a degree of accuracy which is now attainable. A brief description of his method is not out of place. The calorimeter which he used consisted of three concentric cylindrical cans which were insulated from one another by means of air spaces The inner of these cans constituted the calorimeter proper and was made of platinum. The stirrer was a single ring which was moved vertically up and down by mechanical means; since it will be shown in the present work that two such rings vibrating in a similar fashion did not effect thorough mixing, it is quite evident that the stirring which he employed was entirely inadequate The thermometer, which had been carefully standardized, was graduated to tenths and could be read by means of a telescope to 5 one thousandths of one degree—a degree of precision much below the modern standard A single cover on the outside cylinder shielded the apparatus from above and through it the stirrer and thermometer passed The metal was introduced in a sheet or coil of netting, and was withdrawn, washed and dried after a suitable time His results are therefore open to the two main objections, which were emphasized in the introduction, namely, a large cooling correction and an inaccurate method of introducing the metal. Besides these, other sources of error, which must be eliminated from accurate work, were overlooked by him When fine bubbles of gas escape from a solution, they carry away with them small particles of the liquid, and, although the quantity of liquid so carried away is small, yet it is by no means negligible Moreover, his metals were not very pure, being the best he could obtain commercially. The amounts of impurities were determined by analysis, and corrections were applied, entirely ignoring any possible heat effects due to alloying of the metals. The acids mainly used by Thomsen were of two concentrations—$HCl.25H_2O$ and $HCl.50H_2O$. From the results obtained with these acids he calculated the values for acid of the concentration $HCl.200H_2O$. To do this he determined the heat of dilution of the acid from the initial to the final concentration and subtracted the result from the heat of solution of the metal, assuming that the solution of the salt in excess of acid is the same (thermochemically) as its solution in the same quantity of pure water—

---

[1] Thomsen, *Thermochemische Untersuchungen*, Vol. III, page 217. Hess and Favre and Silbermann determined the heats of solution of zinc in hydrochloric and sulphuric acids. Their results have been discussed by Thomsen (*Thermochem. U.*, Vol. III, 273).

an assumption which is plainly hazardous and will be shown later to be incorrect.

A study of one of Thomsen's actual experiments will make clear the error into which he fell as well as indicate the correct method for making this calculation One of the experiments on zinc, in which he dissolved 6 82 grams of zinc in 1248 7 grams of acid of the concentration $HCl.50H_2O$, may be selected[1] The actual conditions of his experiments are accordingly represented by the equation

$$0\ 104Zn + 1\ 332(HCl\ 50H_2O) = \\ 0\ 104H_2 + 0\ 104ZnCl_2 + 1\ 125HCl\ 66\ 6H_2O + 3605\ \text{Cal.},$$

or multiplying by 9 61,

$$Zn + 12\ 80(HCl\ 50H_2O) = H_2 + ZnCl_2(10\ 80HCl)640H_2O + 34{,}620\ \text{Cal.} \quad (1)$$

He then determined the heat of dilution of the acid $HCl.50H_2O$ to $HCl.200H_2O$

$$2(HCl\ 50H_2O) + 300H_2O = 2(HCl\ 200H_2O) + 420\ \text{Cal.}^2 \quad (2)$$

Now by subtracting equation (2) from (1) he claimed to obtain:

$$Zn + 2(HCl\ 200H_2O) = ZnCl_2\ 400H_2O + H_2 + 34{,}200\ \text{Cal.} \quad (3)$$

Evidently this result (equation 3) can only be obtained by a set of reactions similar to the following:

$$\begin{gathered} Zn + 12\ 80(HCl\ 50H_2O) = H_2 + ZnCl_2(10\ 80HCl)640H_2O + x; \\ 12\ 80(HCl\ 50H_2O) + 1920H_2O = 12\ 80(HCl\ 200H_2O) + y, \\ ZnCl_2(10\ 80HCl)640H_2O + 1920\ H_2O - ZnCl_2\ 10\ 80HCl\ 2560H_2O + z; \\ ZnCl_2\ 400H_2O + 10\ 80(HCl\ 200H_2O) = ZnCl_2\ 10\ 80HCl\ 2560H_2O + q; \\ Zn + 2(HCl\ 200H_2O) = ZnCl_2\ 400H_2O + H_2 + x - y + z - q. \end{gathered}$$

That is to say, *all* the acid corresponding to a gram atom of zinc must be diluted, instead of only 2 moles Moreover, the resulting solution of the salt in the excess of acid must be diluted an equivalent amount, and the further change of internal energy, brought about by mixing the pure dilute salt solution (in this case $ZnCl_2\ 400H_2O$) with the proper quantity of acid of equivalent concentration must be determined. It is amazing that no one has ever discovered these errors of logic before. In working out these equations, no account has been taken of the temperature at which the last three reactions should be performed, whether at the initial temperature or final temperature of the experiments for equation (1). This is a matter of considerable importance and will be fully discussed later

Having thus shown the chief causes of inaccuracy in Thomsen's work—which apply with even greater force to earlier experimenters—we may turn to the present series of experiments, and review the various precautions yielding better results. First the preparation of the materials will be discussed, then the calorimetric apparatus, and finally the details of manipulation and the results.

---

[1] *Thermochemische Untersuchungen*, Vol. III, page 272. The mean value 34400+220 c, the heat of vaporization of the water with which the hydrogen was saturated.

[2] *Ibid.*, Vol. III, page 242.

Materials.

The significance of work of this kind depends greatly on the purity of the materials employed. There is, of course, no object in determining accurately the heat of solution of a substance containing unknown impurities in appreciable amount

The materials used in this work were most of them of a high order of purity Where very pure substances were unattainable, the impurities were determined and due allowance for them was made.

Hydrochloric Acid—Three concentrations of hydrochloric acid were used, namely, $HCl\ 8\ 806H_2O$, $HCl\ 20\ 0H_2O$, and $HCl.199\ 8H_2O$. Chemically pure acid was diluted to these concentrations and the exact values were verified by gravimetric analyses in which the chlorine was precipitated with silver nitrate.

Zinc—Two preparations of zinc were employed in the research. The first sample consisted of fine crystals obtained by electrolysis from an ammoniacal zinc sulphate solution A solution containing zinc sulphate had been previously oxidized with chlorine water and the iron precipitated by digestion with freshly made zinc hydroxide. This process was repeated until the precipitate no longer became colored on standing. Zinc sulphate was crystallized from the filtered solution and subsequently recrystallized three times from pure water. The pure salt was dissolved in distilled water, ammonia was distilled into it until the precipitated hydroxide had completely dissolved, and the solution electrolyzed between platinum electrodes under a high current density. In this way very finely divided crystals were obtained, which offered later a large surface to the action of the acid. The metal was removed from the solution by means of a glass instrument resembling a rake, and was preserved under a dilute solution of ammonia. It was washed with dilute ammonia until all zinc salts adhering to it were removed, and immediately afterwards was speedily washed with pure water. As quickly as possible the water was replaced by three washings with alcohol, and this treatment was followed by three more washings with ether.[1] The metal was dried by being placed in a vacuum desiccator containing sulphuric acid.

The surface of the zinc obtained in this fashion, although it appeared very bright, was covered with a very thin film of oxide. This covering was only perceptible from the fact that when thrown upon dry mercury, the metal amalgamated very slowly or not at all; indeed, it could be stirred into the mercury without amalgamating. If, however, the mercury was covered with a dilute solution of ammonia and the zinc thrown upon it, amalgamation proceeded with great rapidity. This fact was utilized to determine the amount of oxide present. A weighed quantity of zinc was amalgamated under a dilute solution of ammonium hydroxide, which was then poured off, neutralized and titrated with a standard potassium ferrocyanide solution. The solution must have contained all the oxide, as the surface of the mercury was perfectly bright. The results show that only a very small part of the metal had been oxidized.

---

[1] The alcohol was purified by being twice distilled from quicklime. The ether was distilled after standing for several days over calcium chloride.

DETERMINATION OF ZINC NOT AMALGAMATED.

	Wt. zinc	Vol. of $K_4Fe(CN)_6$ soln. cc.	Equivalent of zinc oxide. Gram.	Wt. of zinc oxidized in 7.5 grams.
1	1.5	0.14	0.0006	0.0025
2	1.5	0.12	0.0005	0.0020

That is to say, the oxide cannot exceed 0.037 per cent. of the weight taken, hence even if the oxide were insoluble in acid, the error from this source could not exceed this amount. Probably the observed quantity is unduly exaggerated by the solution of some metallic zinc in ammonia, during the act of amalgamation, when electrolytic effects would occur. Therefore 0.03 per cent. is a safe estimate of the combined zinc present in the metal. But a part even of this was probably present as ammoniacal sulphate in solution and not as oxide. When a metal is deposited from a solution, as the zinc crystals had been, it encloses minute drops of the mother liquor, just as do also crystals of most if not all salts;[1] and the quantity of included solution is greater the faster the metal is deposited. The quantity of enclosed mother liquor was determined in the present instance by fusing the metal in a current of dry nitrogen and absorbing the water with phosphorus pentoxide. Blank experiments, in which dry air was passed through the apparatus for a long time, served to eliminate any constant errors of experimentation.

VOLATILE MATERIAL ENCLOSED BY CRYSTALLIZED ZINC.

	Weight of zinc.	Weight gained by pentoxide tube.	Blank.	Weight of volatile matter from zinc.
1	3.00	0.00105	0.0001	0.00095
2	3.00	0.0011	0.0001	0.0010
3	3.00	0.0010	0.0001	0.0009
			Mean,	0.00095

Since the solution used for electrolysis contained about 20 per cent. of zinc sulphate, the total weight of enclosed mother liquor in 3.0 grams of zinc was 0.0012 gram, or 0.04 per cent. of the original weight of metal. This small amount of enclosed mother liquor must have contained about

---

[1] See Richards, *Z. physik. Chem.*, 46, 189 (1903); also Hulett and DeLury, THIS JOURNAL, 30, 1812.

0.1 milligram of zinc, which must have appeared along with the oxidized portion in the amalgamation experiments, and should be subtracted from the quantity there discovered. Otherwise the metal was very pure; a careful qualitative analysis failed to show the presence of any other metal.

The sum total of impurity found in the zinc is thus not over 0 07 per cent., but to apply this correction in full would overstep the mark.

Both zinc oxide and hydroxide, as well as the ammoniacal mother liquor, give out heat when dissolved in acid. The two former yield about two-fifths as much heat as metallic zinc would, and the mother liquor was found to yield about one twelfth as much Hence, considered from a thermochemical point of view, the zinc must have acted as if it contained only about 0 055 per cent of impurity, a correction which is applied in the following pages.

The second sample was Merck's pure zinc ("reagent") in granulated form, which had been pounded into thin sheets on an anvil. Both the hammer and the anvil were carefully cleaned before being used, and the pieces were polished by shaking with sand and alcohol afterwards. This zinc was very pure and contained, as far as careful testing could show, only a very slight trace of iron, which may have been introduced during the process of pounding No attempt was made to determine the amount of iron present, since scarcely a weighable amount of ferric hydroxide was precipitated from seven grams of zinc. No other impurities were found, so that no correction for impurities was made with this material..

Aluminium.—The aluminium used for this work was in the form of a thin foil--the purest that could be obtained on the market. It contained negligible traces of iron and sodium and a small quantity of silicon, which was carefully estimated.

The determination of silicon in a metal of this type is by no means an easy matter. Some of the contaminating element is present in an uncombined form and some combined or alloyed with the metal; the former portion appears as silicon when the metal is dissolved, the latter partly as hydrated silica and partly as hydrogen silicide.[1] The silica is partly precipitated and partly dissolved colloidally. Hence a number of steps have to be taken in order to determine the total amount. In the first place, the aluminium was dissolved in hydrochloric acid and the precipitate collected and ignited in hydrogen. This gave the combined weight of silica and silicon precipitated. Ignition in air then oxidized the silicon to silica, giving a measure of the quantity of the former, and treatment with hydrofluoric acid showed how little of other impurities had been retained by the precipitate. The silica which remained in solution in the acid was found exactly as in a silicate analysis, according to the method recommended by Hillebrand.[1] The silicon which escaped as hydrogen silicide was determined by passing the impure hydrogen from a known weight of the metal through a solution of caustic alkali made from the metal and water in platinum, determining the silica in this solution. Parallel analyses were made with material from several sheets of similar material, the samples showing considerable uniformity. The following tables give the analytical results:

---

[1] Joseph W. Richards.

SILICON IN THE PRECIPITATE.

	Weight of aluminium	Weight of residue after ignition in hydrogen	Weight of residue ignited in air (silica) Milligrams	Per cent of silicon.
1	0.75	....	5.7	0.35
2	0.75	.	5.4	0.33
3	0.75	....	5.1	0.32
4	0.75	0.0030	...	...
5	0.75	0.0030	..	...
		0.0030	5.4	0.34

SILICON IN THE SOLUTION.

Weight of aluminium.	Weight of silica found	Per cent. silicon
0.7500	0.0008	0.050
0.7500	0.0006	0.038
	Average,	0.044

SILICON IN THE GAS.

Weight of aluminium	Weight of silica found.	Per cent silicon.
1.80	0.0008	0.021
1.75	0.0006	0.016
	Average,	0.018

Thus the total weight of the element silicon was found to be 0.40 per cent. of the original weight of the metal taken.

Assuming that the difference between the results of Analyses 1, 2, 3 and 4, 5 gives the weight of oxygen needed to convert uncombined silicon into silica, the silicon present as such in the residue must have been 0.0021 gram.

In computing the effect of the impurity on the heat of reaction, account must be taken of the fact that different forms of silicon have different effects upon the result. According to Berthelot, a gram atom of silicon on being converted into the hydrated dioxide evolves about 180 Calories of heat, whereas it will be seen later that the same weight of aluminium evolves only about 130 Calories. Thus the presence of this silicon causes a larger heat of reaction than the same weight of aluminium. On the other hand, according to Ogier,[1] a gram molecule of hydrogen silicide evolves about 25 Calories when formed from hydrogen and crystalline silicon and 33 Calories when formed from amorphous silicon and hydrogen. When formed from aluminium silicide and hydrochloric acid, the heat of formation would doubtless be somewhat diminished. For the present purpose it is assumed to be about half the value given above, namely, 15 Calories. Making allowance for these facts, it is apparent that for the present purpose the total amount of impurity may be calculated as nearly equal to the amount of silicon found as such, namely, 0.28 per cent.

---

[1] Hillebrand, United States Geological Survey, *Bulletin* 305.

The sodium present was estimated as follows: 0.20 gram of the aluminium foil was dissolved in a platinum dish with pure hydrochloric acid, which gave no test for sodium in the spectroscope; the resulting solution was concentrated to about 1 milliliter and examined in the spectroscope. It was found to be about half as concentrated in sodium as a standard solution which contained 0.02 mg per milliliter. This proves that the quantity of sodium present was less than 0.01 per cent. and may therefore be ignored.

To prepare the metal for use, it was polished on both sides with a mild abrasive; it was then carefully wiped with clean dry cotton and washed with ether to remove any film of grease which may have formed. It was then dried and cut into small pieces with a clean pair of shears.

The metal prepared in this way had a very bright surface and could not have been covered with a film of oxide of more than microscopic thickness. That a film of oxide existed, however, is shown by the fact that the pieces would not amalgamate when thrown on mercury, but if held below the surface of the mercury and scratched, amalgamation slowly occurred. No way was found to estimate the quantity of oxide actually present, because ordinary quantitative analysis could not detect an amount so small. Some idea of the probable quantity, however, may be obtained from the study of the oxidation of electrolytic zinc. The zinc exposed a much greater surface per unit of weight than the aluminium does, and should therefore be oxidized to a greater extent. Now the quantity of zinc oxidized was shown to be less than 0.04 per cent.; nevertheless, when it was thrown on dry mercury and stirred into it, little or no amalgamation took place. As soon as a solution of ammonia was added, however, amalgamation took place almost immediately, and very little zinc was found in the ammonia. It is thus evident that the coating of oxide which will prevent amalgamation is extremely thin; and there is accordingly little likelihood that the film of oxide covering

[1] Ogier, *Ann. chim. phys.* [5], 20, 31, 1880.

the surface of the aluminium was great enough to introduce an appreciable error into the results. In view of these facts the aluminium was assumed to be 99 6 per cent. pure.

Magnesium.—Ribbon—the purest which could be obtained in the market—was used for this work. A careful analysis showed the presence of a small amount of iron and a trace of sodium.

The determination of the iron was made in the following manner: A weighed amount of the metal was dissolved in hydrochloric acid and sufficient ammonium chloride added to prevent the precipitation of magnesium hydroxide. While hot the solution was oxidized with chlorine, and the iron precipitated with ammonia twice in succession, and weighed as oxide The results were as follows:

IRON IN PUREST COMMERCIAL MAGNESIUM.

	Wt. of Mg	Wt of Fe_2O_3	Equivalent wt of iron	Per cent. of iron
1..................	2.50	0 0031	0 0021	0.08
2	2.86	0 0028	0 0020	0.071

Because the iron itself has some heat of solution (about 8 per cent. of that of an equal weight of magnesium), the fraction 0 075 per cent would correspond to about 0 07 per cent. of inactive substance.

The sodium was estimated in the same manner as in the case of aluminium above and was found to be present in about the same quantity. Consequently, no correction for it was necessary.

To prepare the metal for use it was scraped with a knife in order to remove most of its coating of oxide, and afterwards polished with a mild abrasive, which was removed by rubbing with clean dry cotton. The metal then presented a very bright surface and could be kept in a stoppered weighing tube for a long time without tarnishing. There can be no doubt that the surface of the metal was still coated with a very thin film of oxide, because it would not amalgamate when held below the surface of mercury. In view of the experience with zinc, the weight of the oxide probably did not exceed 0 05 per cent. of the weight of the metal. Magnesium, like aluminium, is far more active than zinc, and therefore should be more easily oxidized; but the more compact form probably about compensated in the present case for the greater activity, because less surface was exposed with either aluminium or magnesium than with zinc.

As an outcome of these experiments, the magnesium was assumed to have a purity of 99.9 per cent. with an uncertainty probably not exceeding 0.05 per cent. in either direction.

Cadmium.—The cadmium used for this work was prepared electrolytically from cadmium sulphate which had been twice recrystallized from pure water, in precisely the same way as the zinc. The finely divided crystals were washed with dilute ammonia solution until free from cadmium salt, then with water and finally with alcohol and ether, as before described, and were dried in a vacuum over concentrated sulphuric acid.

Since cadmium is a less active metal than zinc it should be less oxidized when prepared in the same manner. The quantity of zinc oxidized was found to be too small to introduce any serious error into the results. Therefore, the quantity of cadmium oxidized was not determined.

The mother liquor enclosed by the crystals of the metal was found to be considerable in amount, for its determination the method used in the case of zinc was employed.

VOLATILE MATERIAL ENCLOSED BY CRYSTALLIZED CADMIUM

	Weight of cadmium	Weight gained by drying tube	Blank	Weight volatile matter from cadmium
1	5.00	0.00535	0.0001	0.00525
2	5.00	0.00510	0.0001	0.0050
3	5.00	0.0051	0.0001	0.0050
4	5.00	0.0048	0.0001	0.0047
			Average,	0.00499

Since the electrolysis was conducted with a twenty-five per cent. solution, the corrected weight of mother liquor was 0.00665 gram; that is to say, the weight of enclosed mother liquor was 0.13 per cent. of the original weight of metal. The heat produced by the neutralization of this ammoniacal mother liquor was about one sixth of the quantity which would be produced by the solution of an equal weight of cadmium; hence the correction to the weight for thermochemical purposes would be 0.11 per cent. As no other impurity was found in the cadmium, the metal was calculated as having a purity of 99.9 per cent.

Iron.--The iron used in this work was obtained from four different sources.[1] They will be spoken of as Samples A, B, C and D.

Sample A was iron reduced by hydrogen obtained from Kahlbaum and was undoubtedly very pure. It was prepared for use by being freshly reduced in hydrogen, at a very moderate temperature. Ignition at a very high temperature would have diminished the surface and therefore the speed of subsequent solution, by causing the particles to cohere more closely.

---

[1] A fifth sample was furnished by Professor C. F. Burgess, of the University of Wisconsin. It was prepared electrolytically and contained considerable hydrogen. The rate of solution is undoubtedly greatly influenced by the quantity of hydrogen present. When first obtained it dissolved at a rate comparable with the other samples. After having been kept for a year, however, it dissolved so slowly that no results could be obtained with it. The same effect was produced by heating it strongly in a vacuum for a considerable length of time.

We wish to express our thanks to Professor Burgess for his courtesy in supplying this sample.

Sample B was similar in appearance; it was prepared from ferric nitrate which had been recrystallized four times from a strong nitric acid solution. The pure ferric nitrate had been heated in a platinum dish at a low temperature until converted to the dark red basic nitrate. This was then removed, finely ground,[1] and afterwards strongly heated in a platinum dish until completely converted to the oxide. The ferric oxide was placed in a porcelain boat and reduced at as low a temperature as possible in a current of pure hydrogen.[2]

Sample C was made by electrolysis of ferrous sulphate solution, to which had been added a small amount of ammonium chloride. The electrodes were of platinum, and, as soon as a thin layer of iron had formed, it was removed and kept under a dilute solution of hydrochloric acid. In this way thin plates of the metal were obtained, which exposed a considerable surface to the action of the acid The preparation was finally washed with water and reduced in a current of hydrogen.

Sample D was prepared by the electrolysis of a solution of ferrous chloride. It was treated in the same manner as Sample C.

Of these samples, those reduced from pure oxide in hydrogen were undoubtedly the purest; these were essentially free from impurity. The electrolytic iron probably contained less than 0 1 per cent. of impurity derived from the electrolyte.

Apparatus.

The Calorimeter.—This work, involving the purest materials just described, was carried out with the aid of the adiabatic calorimeter, of which a vertical section is shown in the figure. The form of environment first employed consisted of two concentric cylindrical vessels of copper and a cover. The smaller cylinder, within which was placed the calorimeter proper, was secured inside of the larger one on legs made of hollow brass tubes about eight or ten centimeters in length. The space between the copper cylinders was filled with a solution of crude caustic soda, the liquid being allowed to come as near the top of the vessels as possible without danger of overflowing when stirred vigorously. The cover was a cylindrical vessel, also of copper, about ten centimeters in height, of such a diameter that it fitted easily inside the smaller cylinder, and projecting therein to such a depth that it was only two or three millimeters from the top of the calorimeter can. Four vertical brass tubes were soldered into the bottom of the cover, through which passed the stirrer, thermometer, and rod from which the basket containing the metal under treatment was suspended. The cover also was filled with the crude alkaline solution, so that the calorimetric space was surrounded on all sides by an insulating layer of liquid about a decimeter thick, which could be kept by means of added acid so nearly at the same temperature as the calorimeter itself that the exchange of heat between them was negligible. The narrow annular space between the sides of the cover and the top of the inner cylinder was stopped by means of a rubber washer which was fastened to the sides of the cover. If this space was not closed, the current of air circulating through it was found to cause evaporation from the calorimetric vessel, and hence accidental cooling. The liquid in the large outside cylinder jacket was very vigorously stirred by means of a triple-screw propeller—a method which was found to be exceedingly efficient. The cover was stirred by means of a perforated copper disk which moved up and down at the same rate as the stirrer in the calorimeter proper. This method of stirring is not so efficient as the propeller, but was found to be adequate.

---

[1] An iron mortar, according to Hempel, is obviously an ideal tool for this purpose.

[2] Richards and Baxter, *Proc. Am. Acad.*, 35, 253 (1900). *Z. anorg. Chem.*, 23, 245 (1900).

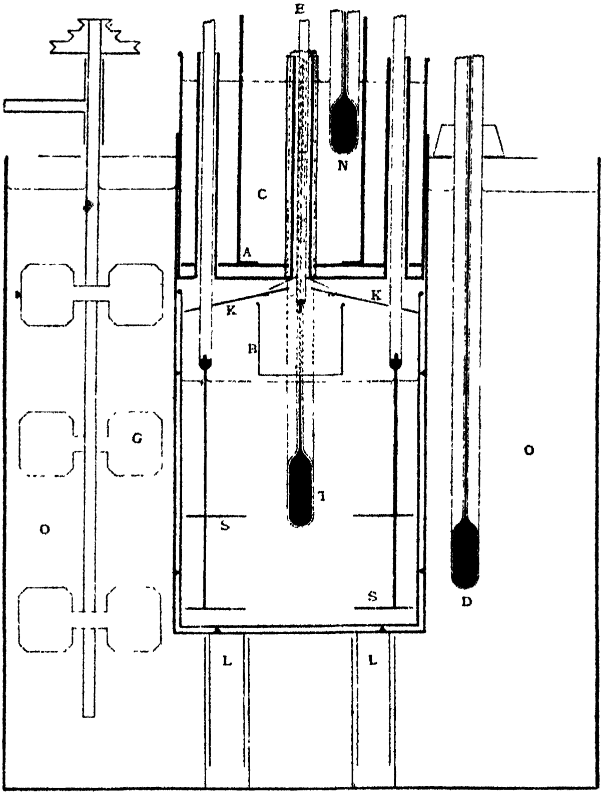


Fig. 1.

A few experiments at the close of the research were conducted by means of a modification of this calorimeter—a modification which on the whole proved so satisfactory that it will be used in future work of this kind. This modification had already been used in principle in the work of Richards and Forbes in "Energy Changes Involved in the Dilution of Zinc and Cadmium Amalgams.[1] In this apparatus the cover of the environing bath was dispensed with, and the calorimeter proper was enclosed in a sealed can of metal wholly below the surface of the liquid in the large copper pail constituting the lower jacket. The tubes for the thermometer and other apparatus were attached to the lid of the sealed can, and the latter was wholly submerged. Thus the reaction was conducted in a sort of submarine vessel, having only a few tubes above the water level.

At first we feared that the cover would be difficult to make water-tight, and that the manipulation would be complicated by the firm attachment of the lid of the calorimeter can, but, as a matter of fact, these difficulties were found not to be prohibitory. By pressing a large flat elastic rubber washer between the top of the can and the lid, and holding the latter down by suitable clamp screws, a perfectly water-tight joint may be had, if the metal surfaces are smooth.

The best arrangement of these details has been described in a paper by R. H. Jesse, Jr., and one of us,[2] in whose investigation the apparatus was subjected to a much more thorough test

A submerged vessel of this kind was found to provide altogether the best means of accomplishing the desired result. With this apparatus the experimenter has only one vessel to adjust at the temperature of the calorimeter inside, and the strain upon him is therefore distinctly less than when the lid also must be specially adjusted. The final results given by the calorimeter are exactly identical with those afforded by the other, as may be seen from the inspection of the results on zinc. The identity with the results obtained with the two sets of instruments is a valuable confirmation of each.

A cylindrical platinum can was used as the calorimeter proper. Its capacity was about 1.2 liters, and it weighed 177.25 grams. It was of such a size that it fitted loosely inside the inner copper cylinder of either form of adiabatic jacket, leaving an air space of about two or three millimeters in width on all sides. From the copper cylinder it was thermally insulated by means of triangular pieces of cork which were made as small as possible and placed with the apex against the calorimeter can. These pieces of cork were so small that their heat capacity was entirely negligible.

Thermometers.—Beckmann thermometers, graduated directly to hundredths and readily estimated to thousandths by means of a lens, were used for determining the temperature change of the calorimeter. They were very carefully standardized by comparison with two international standards, calibrated with the greatest care in Paris.[1] The comparisons were made while the Beckmann thermometers were subjected to precisely the conditions of exposed column, etc., to which they were submitted during the calorimetric determination, so that the corrections could be applied with strict consistency. The cruder thermometers used in the jacket and cover were graduated to twentieths and could be easily estimated to hundredths. They were compared with the standardized thermometers throughout the part of the scale used, and all were set so as to read together within two or three hundredths of a degree.

---

[1] Carnegie Institution of Washington, *Publication* 56, 52 (1906).

[2] THIS JOURNAL, 32, 268.

Stirrers.—In the early parts of the work a stirrer made from round glass rods bent and fused together was used inside of the calorimeter can. The surface exposed by such a system of rods is small, and consequently the stirrer would have to be driven at a high speed in order to produce very complete mixing. As will be shown later, this stirrer was not able, when running at a rate of about one hundred strokes per minute, to stir efficiently the calorimetric liquid. Accordingly, a stirrer made from sheet platinum and offering as great a surface as possible was used in all the final results. The diagram shows clearly the manner of its construction. It consisted of two rings, two centimeters in width, perforated with holes at regular intervals. These rings were connected by rods of platinum, which projected above the surface of the liquid. The rods were sealed into glass tubes which passed through the cover and were connected to the driving mechanism.

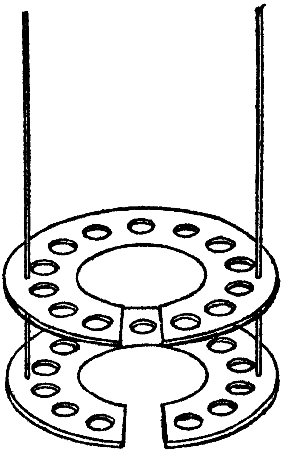


Fig. 2.

The Platinum Basket.—A cylindrical basket, about 4 cm. in diameter and 3 cm. high, made from platinum gauze, was used to support the metal to be dissolved. As the metal was sometimes very finely divided, it occasionally sifted through this gauze, and began to dissolve before its time. In order to prevent this cause of inaccuracy, a cap of platinum foil was sprung over the bottom of the basket outside, and just before the basket was lowered into the acid this cap was pushed off by means of a suitable device and allowed to fall to the bottom of the calorimeter. The basket itself was held by means of a stout hook of platinum wire, attached to the glass tube which ran through the copper tube attached to the center of the cover.

---

[1] These standards are described by Richards and Wells, *Proc. Am. Acad.*, 38, 434 (1902); *Z. physik. Chem.*, 43, 467 (1902).

Apparatus for Preventing Loss of Drops.—In the early experiments a considerable amount of the liquid, as much sometimes as one-half of a gram, was carried away in the form of drops by the escaping gas. These drops resulted, of course, from the bursting of the small bubbles as they rose to the surface. This is a familiar phenomenon whenever a gas escapes from a boiling or effervescing liquid. Several devices were tried to prevent this cause of inaccuracy An inverted watch glass perforated in the center, placed over the top of the basket, served only partially to solve the difficulty. Next, a miniature bell-jar of very thin glass, fitting over the basket, and provided with a fine delivery tube above, just dipping under the liquid, was tested. This device collected the larger bubbles, but the smaller were driven throughout the liquid by means of the violent stirring and escaped from under the bell. Clearly some arrangement was necessary which should include in its scope practically all of the contents of the calorimeter, and, as a matter of fact, the difficulty was entirely overcome by means of such an apparatus as is shown in the accompanying diagram. A large flat cone with a diameter almost as great as the internal diameter of the platinum calorimeter, and an altitude of not over 3 cm , was placed over the basket At the apex a hole was cut to accommodate the rod which carried the basket. The cone was attached to the rod, leaving a space around it for the escape of the hydrogen, and a second small cone fitting closely to the rod was fastened a few millimeters above the first, in order to cover the opening provided for the escape of the gas The fine bubbles of hydrogen slowly ran up the lower sides of the larger cone and collected in larger bubbles under the surface of the smaller cone, and from the edge of the smaller cone the gas bubbled through the liquid in a well-ordered manner, giving a minimum projection of the solution in the form of drops. As the heat capacity of the platinum cones was small and easily determined, this device introduced no error, and at the same time eliminated the difficulty in question. It was used in all the later experiments. Only Series 1, involving the solution of zinc, suffered from loss by the projection of drops, and to this a small correction was applied for the liquid which had escaped being warmed by the reaction in this fashion.

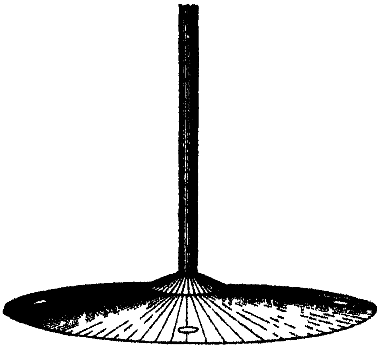


Fig 3.

The Efficiency of Stirring.

It has been stated that previous work of others, as well as our own early experiments, were probably in error on account of inadequate stirring.[1] The facts on which we base this statement will now be presented. In the experiments whose results are tabulated below, three different thermometers were used, all of which had been carefully standardized. No. 1 reached nearly to the bottom of the calorimeter, No. 2 about midway, and No. 3 only a short distance below the surface of the liquid. These three thermometers were used to measure the heat of solution of a definite amount of zinc in dilute hydrochloric acid. The heat capacity of the system was the same in each case and the same weight of metal was dissolved. The liquid was in each case stirred by the inadequate glass stirrer mentioned before. The corrected temperature rise as observed with the three thermometers is recorded in each case.

TEMPERATURE RISE AT DIFFERENT DEPTHS WITH INADEQUATE STIRRING.

	Thermometer No. 1	Thermometer No. 2	Thermometer No. 3
	4.151	4.213	4.225
	4.149	4.210	..
	4.151	4.207	.
	4.150		.
	4.149		....
Mean,	4.150	4.210	4.225

The results with thermometer No. 2 are 1.45 per cent. and that with No. 3 1.8 per cent. higher than those with No. 1, that is to say, the liquid at the top remained consistently warmer than that at the bottom during the experiment, which is exactly what would be expected if the stirring were inefficient. When the thermometer bulb was at the bottom, the temperature indicated by it was undoubtedly too low throughout the whole progress of the experiment. This caused the jacket to be kept at too low a temperature and the reacting system must have lost heat to the surroundings. A parallel error would have come from this cause if the Regnault-Pfaundler method had been used to compute the cooling correction, and has probably entered into much similar work in the past.

After the discovery of this unexpected source of error, the glass stirrer was entirely rejected, and the far more efficient stirrer of platinum alone was used. Experiments were then instituted to discover how rapidly this must be operated in order to commingle adequately the reacting substances. Forty strokes per minute still left an error of over 0.2 per cent., while sixty strokes per minute gave adequate mixing, as judged from the constancy of the outcome. This may be given here, as a contrast to the results in the preceding table. The following results were obtained with two different rates of stirring and two different thermometers. The first thermometer reached about midway, and the second nearly to the bottom of the calorimeter. The heat generated by stirring was determined and in each case the appropriate correction was applied. The values for this correction will be given later. In each case 7.500 grams of zinc were dissolved in 941 4 grams of dilute acid. The nine experiments are arranged below in two ways—first classified as to speed of stirring (Series I and II) and then classified according to the thermometer used (Series III and IV).

---

[1] W. P. White has independently come to the same conclusion, *Phys. Rev.* (1908).

TEMPERATURE RISE AT DIFFERENT DEPTHS WITH ADEQUATE STIRRING.

	Series I. 110 strokes per minute	Series II 60 strokes per minute	Series III. Thermometer 1.	Series IV Thermometer 2
	4.247°	4 246°	4 247°	4 244°
	4.245°	4.245°	4.245°	4.247°
	4.244°	....	4.246°	4.246°
	4.246°	...	4.247°	....
	4.247°	..	4 246°	....
	4.246°	.	4.245°	...
	4.247°	...	....	...
Aver.,	4.2460°	4 2455°	4.2460°	4.2457°

These results prove conclusively that with the rates of stirring employed the mixing was very complete and the liquid was uniformly warmed throughout the reaction, for the differences between each average and the general average are of the same order as the probable error of each. In other words, the results are identical within the limits of experimentation. Hence the rate of sixty strokes per minute was adequate, with our efficient stirrer, to accomplish the desired result

Correction for Heat Evolved by Stirring.

The rate of stirring required for these experiments was sufficient to cause considerable heat to be generated. This quantity must obviously be determined for each liquid used. In the adiabatic calorimeter the determination may be made with great ease and precision.

When the acid solution ($HCl.20H_2O$) was stirred at the highest rate employed, *i. e.*, 110 strokes per minute, the following results were obtained:

	Time. Min	Temperature rise	Average rise per minute
1.	20	0.025°	0.00124°
2.	15	0.018°	0.00120°
3.	30	0.038°	0.00125°
Total.	65	0.081°	0.00123°

When the more concentrated acid ($HCl.8.808H_2O$) was stirred at the same rate, a rise of 0.054° was caused in 30 minutes, at the rate of 0.0018° per minute. Thus the denser liquid caused a greater stirring correction, partly because of its lower heat capacity.

With the same acids and the slower rate of stirring (60 strokes per minute) the correction assumed the following much smaller values;

Acid.	Time. Min.	Temperature rise.	Average rise per minute.
$\mathrm{HCl.8.808H_2O}$	60	0.009°	0.00015°
$\mathrm{HCl.20H_2O}$	40	0.006°	0.00014°
$\mathrm{HCl.20H_2O}$	60	0.008°	0.00014°

The value for the least concentrated acid ($\mathrm{HCl.200H_2O}$) was not determined, but since the heat capacity of the system in that case was about 10 per cent. greater than that with the acid ($\mathrm{HCl.20H_2O}$) the stirring correction was undoubtedly about 0 007° in an hour. It is interesting to note that when the rate of stirring is doubled the heat generated is increased about tenfold. This is in approximate agreement with experience of naval engineers in calculating the quantity of coal necessary to drive ships at sea.

Possible Error Caused by Heat Exchange with Surroundings.

If the environment of the calorimeter is kept *exactly* at the temperature of the calorimeter, no heat exchange can take place. Since perfect exactness in this adjustment is not often to be attained, we investigated with care the possible effect of slight imperfections in the adjustments of temperatures We had expected to find nearly equal effect in the two opposite directions of cooling and warming, but somewhat to our surprise, this expectation was not fulfilled. When the temperature of the jacket was maintained 0.1° higher than that inside the calorimeter for a period of twenty minutes, only a barely appreciable change was observed in the temperature inside the calorimeter; but when it was 0.1° lower a very noticeable cooling effect is manifested. This latter effect was proba- due to a distillation of the water out from the calorimeter and subse- ent condensation on the copper walls of the inside of the jacket. Dis- lation into the calorimeter when the outside jacket was warmer could ot take place, because the calorimeter space is entirely protected from he outside air, and there was then no source of moisture to draw upon. t is possible that evaporation into the slight current of air drawn through the tubes also contributed to the effect.

This observation, which was first made by one of us in collaboration with Dr. A. W. Rowe, is so important in its bearing upon calorimetric work in general that a typical series of results should be given. In the first place, the outer jacket was adjusted at precisely the same temperature as the calorimeter, and the small correction for the stirring of the latter was noted. The jacket was then kept at a temperature just 0.1° above the calorimeter, and the further progress of the temperature was carefully observed. Two rates of stirring were employed in two different experiments, one very active, and the other somewhat less so. Having thus determined the effect of having the jacket too hot, the same experiment was repeated with the opposite disturbing cause—the jacket around the calorimeter was kept 0 1° too cool. The results are recorded in the table below; in each case the test lasted forty minutes:

EFFECT OF MAINTAINING JACKET AT TOO HIGH OR TOO LOW A TEMPERATURE.

Rate of stirring	Correction for stirring for time named	Excess of jacket temperature	Change in calorimetric temperature	Effect to be measured.
Rapid	0.006°	+0 1°	+0.008°	+0.002°
Slow	0.002°	+0.1°	+0 004°	+0 002°
Rapid	0.006°	—0 1°	—0 018°	—0.024°
Slow	0 002°	—0.1°	—0 021°	—0.023°

Thus each set of experiments is entirely consistent within itself; clearly, the exposure of the calorimeter to an environment warmer by 0 1° only alters the temperature of the former by 0 001° in twenty minutes; but if the difference of temperature is in the opposite direction, the cooling correction is more than ten times as great

These experiments demonstrate the faultiness of Rumford's method of correcting for cooling by starting a reaction as much below the temperature of the room as the process concludes above it. Evidently, if the calorimeter is in a closed metal vessel like ours, the gain in heat during the first part of the process will be only about one-tenth as great as the loss during the latter part, and the total observed evolution of heat will be much too small. Because Rumford's method has usually been used in the case of the solution of metals in acids, the discovery of this source of error is especially pertinent to the present work.

After the discovery of these circumstances the temperature in the jacket is always kept one or two hundredths of a degree above rather than a little below that in the calorimeter. There was no difficulty in keeping the temperature of the jacket within 0 1° of that of the calorimeter throughout an experiment, and for the greater part of the time the difference was 0 05° or less, hence it is evident that no error is introduced in the present case from this source. The stirring correction was determined under precisely similar conditions, and hence could be consistently applied.

Correction for Evaporation of Acid.

The hydrogen evolved during these reactions is saturated with the vapor of the solution in which it is produced. Others have considered it as saturated with aqueous vapor only, and the correction has been calculated, assuming that the heat of evaporation of water was the same from an acid solution as from pure water. We thought it worth while to test this assumption by experiment, and the following account of the test may well be given here following that of the other small corrections, although the application of the results is not in place until the completion of the chief part of the experiment.

The test was conducted by bubbling dry air through the usual amounts of the various solutions concerned, kept at the average temperature of the main experiment, and noting the fall of temperature actually produced per liter of air.[1]

The details of experimentation were as follows: Into an eight-liter roughly graduated bottle was run a stream of water, thus forcing the imprisoned air through the driers, which consisted of two sulphuric acid wash bottles and a phosphorus pentoxide tube. The air subsequently passed through a long coil of lead pipe in the calorimeter and a shorter coil in the cover, to ensure that the air should be at the same temperature as the liquid inside. It then passed through a central tube of the cover and bubbled through the liquid inside the calorimeter. In order to prevent the absorption or emission of an appreciable amount of heat by the air in passing through that very small part of the tube exposed to the air of the room, the latter was kept as near the temperature of the experiment as possible

A thermometer was placed in the bottle to measure the temperature of the air at the beginning of the experiment, and a mercury gauge also was inserted to indicate the difference in pressure. The volume of the air was corrected to standard conditions. In order to test the accuracy

	Liquid	Heat capacity of system in Calorie units	Initial temp of exp	Corrected volume of air in liters	Observed fall of temperature	Correction for heat by stirring	Corrected fall	Average per liter.
1	Pure water ..	913	18.0°	6.62	—0.063°	—0.005°	—0.068°	—0.0101°
2	" ...	913	18.0°	7.40	—0.074°	—0.005°	—0.079°	—0.0105°
							Mean,	—0.0103°
3 1	$HCl.200H_2O$ ..	900	17.6°	7.60	—0.074°	—0.005°	—0.079°	—0.0105°
4 2	" ..	900	18.0°	7.47	—0.076°	—0.005°	—0.081°	—0.0107°
5 3	" ..	900	18.0°	7.42	—0.073°	—0.005°	—0.078°	—0.0105°
							Mean,	—0.0106°
4	$HCl.20H_2O$ ...	814	18.0°	7.47	—0.082°	—0.006°	—0.088°	—0.0117°
5	" ...	814	17.9°	7.48	—0.083°	—0.004°	—0.087°	—0.0116°
6	" ...	814	17.7°	7.56	—0.085°	—0.005°	—0.090°	—0.0118°
							Mean,	—0.0117°
7	$HCl.8.8H_2O$ ..	732	18.0°	7.41	—0.048°	—0.006°	—0.054°	—0.0073°
8	" ..	732	18.1°	7.38	—0.053°	—0.005°	—0.058°	—0.0077°
							Mean,	—0.0076°

---

[1] Dry hydrogen would perhaps have been better, but we assumed that the same quantity would evaporate into each gas.

of the method, pure water was at first experimented upon, and the results are given in the table above, with those concerning the acid. The table explains itself; attention is called to the fact that the last column contains the essential outcome of the experiment, namely the cooling effect produced on the given calorimetric system by evaporation into a single liter of dry gas. The mean temperature of the other experiment (18°) was chosen for these experiments.

Evidently the cooling effect produced in pure water and the two most dilute solutions of hydrochloric acid is almost the same, allowing for the somewhat different heat capacities of the two systems, as indeed one would expect; but with the most concentrated acid the cooling effect is very much less in proportion. On comparing the actually observed cooling effects with those calculated from the tension and latent heat of pure aqueous vapor at the appropriate temperatures (0.0098°, 0.0099°, 0.0109° and 0.0121°, respectively), it is apparent that in every case except the last the method gives a higher result than the theoretical one by an amount averaging about 5 per cent. This is undoubtedly in part due to the cooling effect produced by the expansion of the gas, as it rises through the liquid, but this effect is not large enough to account for the whole difference. The discovery of the cause of irregularity would have constituted a research in itself, and as an accuracy of 5 per cent. was enough for our present purpose, the matter was not followed further at this time. The diminished cooling effect in the most concentrated acid is the important outcome of this series of experiments.

The Heat of Solution of Metals in Concentrated Acids.

The heats of solution of the metals, zinc, aluminium, magnesium, cadmium, and iron have all been determined in the course of the present research, and so also have the heats of dilution of the liquid factors and products concerned, in order that all the results might be reduced to the usual dilution with 200 molecules of water. The present section deals with the determination of the heat of solution.

In each case (except a few of the experiments with magnesium) enough metal was used to cause in the calorimetric system employed in its particular case, a change of temperature of about 4°, and in each case the final temperature was not far from 20°, the range being from the neighborhood of 16° to that of 20°. Because of the widely different speeds of reaction with these five different metals, different concentrations of acid were needed in the different cases in order that the reaction should neither be too rapid nor too slow in rate. For zinc and aluminium the concentration $HCl.20.0H_2O$ was used; for the magnesium a solution in ten times as much water ($HCl.199.8H_2O$); and for cadmium and iron, which dissolved much more slowly, the far more concentrated solution, $HCl.8.808H_2O$ was needed, and even this acted with extreme slowness.

Stronger solutions were not used because of the large amount of acid which evaporates from them, and because of the excessive complication introduced by the great heat of dilution. Hydrochloric acid was used rather than sulphuric because there is no danger in the case of hydrochloric acid of the existence of such side reactions as are caused by the partial reduction of sulphuric acid

The method of experiment was essentially the same in the case of each metal. A weighed quantity of acid was placed in the calorimeter and a weighed quantity of metal in the basket. The whole apparatus was then assembled in the manner shown in the diagram (Fig. 1). The temperature of the jacket and cover were adjusted to that of the calorimeter, and the whole was allowed to stand for ten or fifteen minutes to make sure that the basket and metal had reached the temperature of their surroundings The stirrers were put in motion, and the thermometer was read until a constant reading was obtained for several minutes. The basket was then lowered into the acid and the rise of temperature inside equaled in the jacket by running concentrated sulphuric acid from the burettes. These burettes were graduated in tenths of a degree—that is to say, they indicated the amount of acid necessary to raise the alkaline solution in the jacket by successive increments one-tenth of one degree. The reaction of course became slower and slower, as it proceeded, and finally, when the temperature rise settled down to the regular rise due to the known correction for the stirring, the reaction was known to be at an end, and the final temperature readings were made.

As will be seen from the table below, the time necessary varied greatly in the different cases, depending in part upon the accidental arrangement of the pieces of metals in the basket and in part upon their chemical nature. In the cases of cadmium and iron, the reactions were so deliberate that it was necessary to introduce platinum chloride into the solution in order to catalyze the reaction. This resulted, of course, in a side reaction, involving the deposition of a small amount of platinum and the corresponding evolution of slightly too much heat. The platinum so deposited was collected by filtration and was weighed at the close of the experiment. The correction was applied duly in each case, and amounted on the average to somewhat less than four one-thousandths of a degree in the case of iron, the average amount of platinum precipitated in each case being about 8 milligrams in the case of cadmium and 10 milligrams in the case of iron. The equations necessary for calculating the reaction for the platinum precipitated by cadmium are as follows:

$$\mathrm{Pt} + 2\mathrm{Cl}_2 + 2\mathrm{HCl\ aq} = \mathrm{H_2PtCl_6\ aq} + 84.6\ \mathrm{Cal};^{1}$$

---

[1] Thomsen, *Thermochemische Untersuchungen*, 3, 431 (1883).

$$2Cd + 2Cl_2 + aq = 2CdCl_2\,aq + 192.5\text{ Cal};^{1}$$

$$2Cd + 2H_2PtCl_6\,aq = 2CdCl_2\,aq + Pt + 2HCl\,aq + 107.9\text{ Cal.}$$

By subtracting from this the value for the reaction $2Cd + 4HCl\,aq = 2CdCl_2\,aq + 2H_2 + 35.0$ Cal., we obtain the quantity of heat which is introduced by the action of one gram-atom of platinum, *i. e.*, 73 Cal. The correction was calculated by means of the following formula:

$\beta = 73 \times W/M \times K$, where β = correction in thousandths of one degree, W = weight of platinum found, M = atomic weight of platinum, and K = heat capacity of system.

The equations used in calculating the correction for platinum precipitated by iron are as follows:

$$Pt + 2Cl_2 + 2HCl\,aq = H_2PtCl_6\,aq + 84.6\text{ Cal.}$$

$$2Fe + 2Cl_2 + Aq = FeCl_3\,aq + 199.9\text{ Cal.}^{2}$$

$$2Fe + H_2PtCl\,aq = 2FeCl_2\,aq + Pt + 2HCl\,aq + 115.3\text{ Cal.}$$

Subtracting from this the heat of solution of two gram-atoms of iron:

$$2Fe + 4HCl\,aq = 2FeCl_2\,aq + 2H_2 + 42,$$

gives the output of heat (73 Cal.) for one gram atom of platinum. The correction is calculated by means of the equation already given, the evolution of heat being essentially identical in the two cases. A portion of the liquid was removed with a pipette immediately at the close of the experiment and tested with sulphocyanate; no trace of oxidation was observed.

The heat capacities of the various factors in the reaction, including the calorimetric apparatus which was warmed by it, were computed from the weights of the several parts. By far the most important portion of the heat capacity consists of the acid solution, and accordingly, especially accurate determinations were needed. We are greatly indebted to Dr. A. W. Rowe for his kindness in determining the specific heats of the three acids used by us between the temperatures of 16° and 20°, by the new method now in use in Harvard University.[3] The specific heats of the three acids employed were respectively as follows: the weakest solution ($HCl.199.8H_2O$) 0.9814, the solution of medium concentration ($HCl.20.0H_2O$) 0.8486, the most concentrated solution ($HCl.8.808H_2O$), 0.7312, compared with water over the same range, 16 to 20°. The specific heats of the various pieces of apparatus (with the exception of the thermometer) and the metal dissolved are given with sufficient accuracy by previous determinations made by others and were taken as follows:

---

[1] Thomsen, *Thermochemische Untersuchungen*, 3, 284 (1883). For the sake of consistency Thomsen's somewhat crude figures were used throughout.

[2] *Ibid.*, 3, 287.

[3] Ric[illegible] Rowe, *Proc. Am. Acad.*, 43, 475 (1908); *Z. physik. Chem.*, 64, 187 (1908).

Zn	0.098	Fe	0.112
Al	0.202	Pt	0.032
Mg	0.245	Glass	0.186
Cd	0.054		

The thermometer was estimated by the method given in Ostwald-Luther's well-known "Handbuch."[1] The following table gives the heat capacities of the various systems concerned. The two series of experiments with zinc differ only in that the first series was conducted with the inadequate glass bell for preventing the projection of drops of liquid. Accordingly the specific heat of 25 grams of glass had to be included in the system, and a correction of one quarter of a gram had to be made for the liquid lost by projected drops of liquid. The amount of this loss was found to be on the average about one half a gram, and one-half of this quantity was taken, because the loss was gradual from the beginning to the end of the experiment. In the second series with zinc and all the other series with other metals the platinum cone, weighing about 9 grams, replaced the inadequate glass bell, and no important amount of acid was lost by the projection of drops. The differences in the heat capacities of the acids are due to the different specific heats and weights taken. The system included also half of the air in the space surrounding the calorimeter by means of which the latter was insulated from the inner cylinder of the jacket. The volume of air was calculated to be 160 cubic centimeters, which at constant pressure has a heat capacity of 0.22 mayer. Since the total heat capacity of the system was always over 3000 mayers, this quantity may safely be neglected, as being beyond the accuracy of the measurement.

In the first three experiments with zinc, 941.2 grams of acid were used; in each of the other experiments with zinc and aluminium the weight of acid was 941.4 grams. In the case of magnesium, 904.0 grams of the more dilute acid were employed, while the most concentrated acid used in the experiments with cadmium and iron, weighed 983.0 grams in each trial. Here is given a table showing the heat capacities of the several systems, calculated from the foregoing data.

	First zinc.	Second zinc.	Aluminium	Magnesium.	Cadmium	Iron.
Platinum	8.4	8.7	8.7	8.7	8.7	8.7
Glass	4.7	...	..	...	...	...
Acid	798.7	798.9	798.9	887.2	718.8	718.8
Metal	0.7	0.7	0.2	0.2	0.8	1.0
Thermometer	1.4	1.4	1.4	1.4	1.4	1.4
Total in Cal/t°	813.9	809.7	809.2	897.5	729.7	729.9
Total in mayers	3404.	3386.	3384.	3753.	3053.	3053.

---

[1] Ostwald-Luther, "Hand- und Hülfsbuch zur Ausführung physikochemischer Messungen," 2nd edition (1902).

With successive preparations of each of these systems a number of experiments on the heat of solution of metals in acids were made. More experiments were made with zinc than with the other elements for three reasons: in the first place because the first method which had been used was not wholly satisfactory, in the next place because experience was at that time being gained concerning all the details of the manipulation, and finally because two entirely different samples of zinc were tested.

The volume of hydrogen evolved in each of these experiments under standard conditions was calculated, and multiplied by the average fall in temperature per liter of gas passed through each calorimeter full of each acid, according to the table already given on page 451.

A sample experiment showing the general method is given below.

The Heat of Solution of Zinc.

7 5 grams of electrolytic zinc were used, being equivalent, according to the analysis, to 7 496 grams of pure zinc. The calorimeter contained 941.4 grams of acid or 2.372 moles of hydrogen chloride. The temperature of the air was 18°. This is the experiment number 6 below.

Time.	Reading of thermometer in calorimeter	Reading of thermometer in the jacket reduced to the same standard as the calorimeter.	Reading of the thermometer in the calorimeter corrected for errors of calibration.
0	0.830	0.82	0.808
1	0.830	0 82	0 808
2	0.830	0 85	0.808
3	0.830	0.85	0.808
20	5.010	5.02	5.027
22	5.031	5 04	5.049
23	5.033	5.08	5.051
24	5 035	5.09	5.053
25	5.035	5 05	5.053
26	5.035	5 05	5.05
27	5.036	5.04	5.054
28	5.036	5 02	5.054

Thus the difference between the corrected readings of the thermometer was 4.246. To this must be added 0.002° for the correction for the thread of the thermometer exposed to the somewhat cooler air of the room, and from the results must be subtracted 0 003° for the heat added by the stirring, the slower rate having been used in this experiment. The final temperature attained was 19.87°. The volume of hydrogen evolved, reduced to standard conditions, was 2.57 liters, which number being multiplied by the cooling effect of one liter of gas under the same conditions (0 0117°), gives 0.030°, the correction to be applied for the vaporization of the solution. The corrected rise of temperature is 4 275° in a heat capacity of 809.7. Multiplying these two quantities together, the heat evolved in the experiment, expressed in 18°-Calories, is found to be 3461 Calories. A table containing the data for all the metals follows:

DATA CONCERNING THE HEAT OF SOLUTION OF FIVE METALS IN HYDROCHLORIC ACID AT 20°.

No. of exp.	Designation.	Corr. weight of pure metal. Gms.	No. of moles of HCl in calorimeter	Duration of exp.	Corr. change of thermometer reading	Corr. for heat by stirring	Corr. for solvent vaporized by hydrogen	Corrected rise of temperature.	Heat capacity of system in Cal/T°	Heat evolved in experiment (in 18° calories).
1	Zn (A)..........	7.496	2.372	37	4.268°	—0.046°	+0.030°	4.252°	813.9	3461
2		7.496	2.372	20	4.245°	—0.025°	+0.030°	4.250°	813.9	3459
3		7.496	2.372	24	4.248°	—0.029°	+0.030°	4.249°	813.9	3458
4		7.496	2.372	17	4.268°	—0.021°	+0.030°	4.277°	809.7	3463
5		7.496	2.372	12	4.260°	—0.014°	+0.030°	4.276°	809.7	3462
6		7.496	2.372	25	4.248°	—0.003°	+0.030°	4.275°	809.7	3461
									Average,	3461
7	Zn (B)..........	7.500	2.372	18	4.269°	—0.022°	+0.030°	4.277°	809.7	3463
8		7.500	2.372	16	4.267°	—0.020°	+0.030°	4.277°	809.7	3463
9		7.500	2.372	15	4.249°	—0.002°	+0.030°	4.277°	809.7	3463
10[1]		7.500	2.372	22	4.249°	—0.003°	+0.030°	4.276°	809.7	3462
									Average,	3463
11	Al..............	0.747	2.372	55	4.296°	—0.008°	+0.008°	4.296°	809.2	3475
12		0.747	2.372	23	4.287°	—0.003°	+0.008°	4.292°	809.2	3473
13		0.747	2.372	20	4.289°	—0.003°	+0.008°	4.294°	809.2	3475
14		0.747	2.372	26	4.287°	—0.004°	+0.008°	4.291°	809.2	3472
15		0.747	2.372	25	4.288°	—0.004°	+0.008°	4.292°	809.2	3473
16		0.747	2.372	23	4.291°	0.003°	+0.008°	4.296°	809.2	3475
									Average,	3474

---

[1] This experiment was performed with the submarine apparatus; all others with the original form of calorimeter.

DATA CONCERNING THE HEAT OF SOLUTION OF FIVE METALS IN HYDROCHLORIC ACID AT 20° C—(*Continued*).

No. of exp.	Designation.	Corr. weight of pure metal. Gms.	No. of moles of HCl in calorimeter.	Duration of exp.	Corr change of thermometer reading	Corr. for heat by stirring.	Corr. for solvent vaporized by hydrogen.	Corrected rise of temperature.	Heat capacity of system in Cal/1°.	Heat evolved in experiment (in 18° calories).
17	Mg.............	0.8492		22	4.283°	—0.003°	+0.008°	4.288°	897.5	3848
18		0.8492		22	4.278°	—0.002°	+0.008°	4.284°	897.5	3845
19		0.8492		23	4.279°	—0.002°	+0.008°	4.285°	897.5	3846
20		0.4246		20	2.140°	—0.002°	+0.004°	2.142°	897.4	1922
21		0.4246		21	2.141°	—0.002°	+0.004°	2.143°	897.4	1923
22		0.4246		24	2.143°	—0.002°	+0.004°	2.145°	897.4	1925
	Average,	0.8492							Average,	3846
23	Cd.............	14.983	5.038	29	3.594°	—0.009°	+0.022°	3.607°	729.7	2632
24		14.983	5.038	49	3.604°	—0.012°	+0.022°	3.614°	729.7	2637
25		14.983	5.038	51	3.594°	—0.006°	+0.022°	3.610°	729.7	2634
26		14.983	5.038	41	3.664°	—0.077°	+0.022°	3.609°	729.7	2634
27		14.983	5.038	21	3.632°	—0.040°	+0.022°	3.614°	729.7	2637
									Average,	2635
28	Fe, A...........	9.000	5.037	94	4.530°	—0.019°	+0.027°	4.538°	729.9	3312
29	A...........	9.000	5.037	166	4.533°	—0.026°	+0.027°	4.534°	729.9	3309
30	B...........	9.000	5.037	97	4.528°	—0.018°	+0.027°	4.537°	729.9	3312
31	B...........	9.000	5.037	43	4.513°	—0.005°	+0.027°	4.535°	729.9	3310
32	C...........	9.000	5.037	109	4.538°	—0.025°	+0.027°	4.540°	729.9	3314
33	D...........	9.000	5.037	235	4.553°	—0.040°	+0.027°	4.540°	729.9	3314
									Average,	3312

The table explains itself, the five metals, zinc, aluminium, magnesium, cadmium, and iron being named in the order in which they were investigated in the second column, and the various essential data concerning the several experiments being given in the following columns. The last column of all contains the products of the several parts of numbers in the two preceding columns and gives the various amounts of heat evolved in each of the several experiments. These values are those which would be manifested by an isothermal reaction conducted at the final temperature attained in each case, 20° ±, because the heat capacities of the factors were used in calculating the results.[1]

Comparison of the results in the last column of this table shows that the calorimetric method had been brought to a high degree of constancy, because the agreement between the several results for each reaction is excellent; that is to say, the probable error of each of these averages is small, in so far as the actual errors of experimentation are concerned. Except in the case of cadmium, which is the least satisfactory, the maximum difference from the mean of the individual determinations is very little over one-twentieth of one per cent., and even in the case of cadmium it is only about one-tenth of one per cent. The probable error calculated according to the method of least squares is accordingly much less than this. Evidently we have here a list of data far more accurate than anything of the kind which has been published before. For example, Thomsen's results for zinc, with which he made more experiments than in the other cases, vary from 34.04 to 34.69 Calories—an extreme variation of nearly 2 per cent., or a deviation from the mean of about 1 per cent. on each side. This is a grade of accuracy over tenfold less than that shown by the present series of determinations. The average final results are brought together in the following table, together with the same calculated upon the basis of a gram-atom of metal instead of the small amount which happened to be used in the experiment. The latter are given both in terms of large Calories (18°) and kilojoules, the factor 4.182 being employed for the computation of kilojoules. The range over which the specific heats were measured being 16–20°, the Calorie is taken at 18°.

HEAT OF SOLUTION OF THE METALS IN AN EXCESS OF HYDROCHLORIC ACID AT 20°.

Metal.	Concentration of acid.	Weight of metal dissolved	Heat evolved in experiment (in small Calories).	Atomic weights	Heat evolved for 1 gram atom of metal.	
					In large Calories (20°).	In kilojoules.
Zn +	$HCl.20H_2O$	7.496	3462	65.37	30.19	126.8
Al +	$HCl.20H_2O$	0.7470	3474	27.1	126.0	527
Mg +	$HCl.200H_2O$	0.8492	3846	24.32	110.15	460.6
Cd +	$HCl.8.8H_2O$	14.985	2635	112.42	19.77	82.68
Fe +	$HCl.8.8H_2O$	9.000	3312	55.85	20.55	85.94

---

[1] Richards, THIS JOURNAL, 25, 209 (1903).

The direct comparison of these numerical values with Thomsen's is not immediately possible, because in all cases the acid used by us was of a different concentration from that used by him. It has already been shown that Thomsen's method of calculating for more dilute acids was erroneous, so that only his actual uncorrected results with acids more concentrated than $HCl.200H_2O$ are worthy of consideration.

An essential part of the research, without which the results recounted in the present paper are incomplete, is therefore the precise determination of the heats of dilution of the several acid solutions concerned. This work has already been almost finished, awaiting only a few final determinations for completion. The details will soon follow in a second paper.

Summary.

1. The new method of adiabatic calorimetry was applied to the solutions of metals in acids. The method is particularly adapted to the determination of the energy change involved in these reactions on account of the length of time required by them.

2. The faults in the old method of estimating the weight of metal dissolved are pointed out and a method of avoiding them is described.

3. It has been shown that in order to insure the complete equality of temperature during the reaction, the stirring within the calorimeter must be very vigorous. All the previous results are probably in error from lack of this knowledge.

4. The quantity of heat generated by stirring a liquid is shown to be increased nearly 10 times when the rate of stirring is doubled.

5. The cooling effect of the evaporation of the acid solution into the escaping hydrogen has been directly evaluated and a suitable correction applied.

6. The quantity of oxide on the surface of the metals employed was shown to be extremely small, and the purity of the materials was carefully investigated, suitable corrections being applied when necessary.

7. The heats of solution of the metals zinc, aluminium, magnesium, cadmium, and iron in hydrochloric acid were determined.

8. The error in Thomsen's method of calculating the heat of solution of a metal in dilute acid from the data obtained with concentrated acid is pointed out.

9. The second part of this paper, containing the essential heats of dilution concerned, will follow soon.

THE CHEMICAL LABORATORY OF HARVARD COLLEGE,
CAMBRIDGE, MASS., U. S. A., 1907-1909.

AN ADIABATIC CALORIMETER FOR USE WITH THE CALORIMETRIC BOMB.

BY FRANCIS G. BENEDICT AND HAROLD L. HIGGINS

Received January 24, 1910

The calorimeters generally used with the calorimetric bomb are subject to error due to thermometer lag and exchange of heat with the surrounding media. The thermometer lag is seldom taken into consideration, although Richards[1] shows it is likely to be the cause of a considerable error. The exchange of heat with the surrounding media involves the use of an elaborate, time consuming, cooling correction, which can hardly gauge the loss of heat with any great accuracy. If, however, the calorimeter is rendered adiabatic by keeping the media surrounding it always at the same temperature as the calorimeter itself, both of these errors are avoided.

In 1895, in applying calorimetry to experiments on man, Rosa[2] constructed a large chamber which was made adiabatic by arbitrarily cooling and heating an outer zinc wall to correspond with the fluctuations in temperature of the copper wall of the calorimeter proper. By this method any interchange of heat was avoided and the principle has been found very satisfactory in respiration calorimeters. In connection with the respiration calorimeter at Wesleyan University, considerable work was done with the calorimetric bomb, including the production of a modification of the Berthelot bomb.[3] Experiments were also made there by one of us in an attempt to apply adiabatic conditions to the bomb calorimeter. To this end, special forms of apparatus for heating electrically a surrounding water jacket were employed, but owing to the difficulty in properly insulating the heating wires, the experiments proved unsuccessful. Meanwhile the excellent apparatus of Richards, Henderson and Frevert[4] appeared, an adiabatic calorimeter which is admirably designed for the special purposes for which it has been used in Richards' laboratory and which leaves nothing to be desired in regard to accuracy. For practical purposes, however, it is somewhat cumbersome and involves the use of rather large amounts of strong alkali and acid.

On installing a calorimetric bomb at the Nutrition Laboratory for use in measuring the potential energy of food, feces, and urine, experiments were continued to obtain a practical form of adiabatic calorimeter in which the temperature of an outer water jacket should be controlled by electric heating, and the apparatus here described was devised.

Description of Apparatus.—The calorimeter system, the rise in temperature of which gives the data for computing the number of Calories produced during a combustion, is shown in the figure and consists of the bomb A, the calorimeter can B, and the water it contains, the stirrer, and the immersed portion of the thermometer. In our development of

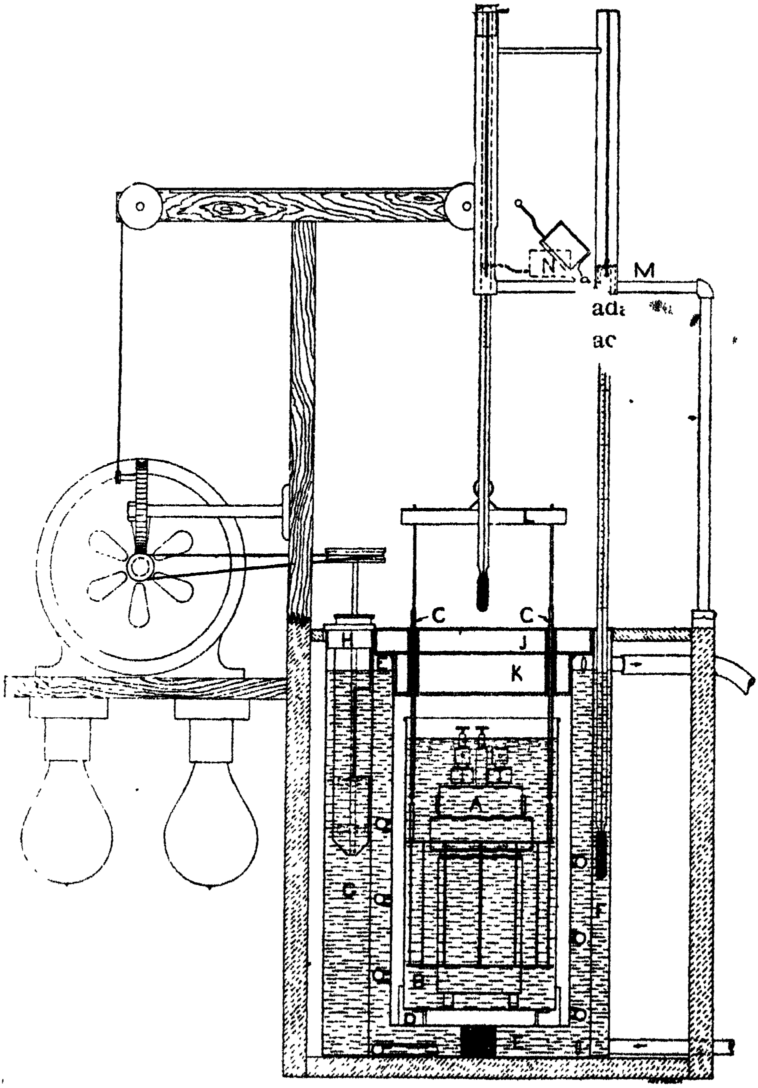
---

[1] Richards, Henderson and Forbes, *Proc. Amer. Acad. Arts and Sci.*, 41, No. 1 (May, 1905).

[2] Atwater and Rosa, *Physical Rev.*, 9, Nos. 3 and 4 (1899).

[3] Atwater and Snell, THIS JOURNAL, 25, 659 (1903).

[4] Richards, Henderson and Frevert, *Proc. Amer. Acad.*, 42, No. 21 (March, 1907).



the calorimeter, we have used for the most part a Kröker bomb, but the calorimeter is applicable to any type of bomb with which we are familiar. The calorimeter can is of nickel-plated brass (24 cm. high and 13 cm. in diameter), being 13 mm. higher than the bomb. The stirrer consists of two flat brass rings, encircling the bomb, perforated by a number of holes, and held together by several small brass rods 10 cm. long. This stirrer is connected with the mechanism for raising and lowering it by two rods, C C, which are made of hard rubber to prevent conduction of heat from the calorimeter. On both of these rods, brass eye-joints are used which allow the stirrer flexibility of motion and prevent it from binding. The calorimeter can rests on three hard rubber guides and knife edges, D, within a second can, about 13 mm. of air space surrounding the calorimeter can on all sides.

To prevent the calorimeter system from exchanging heat with the surrounding media, it is placed inside of a water jacket, E, which is always maintained at the same temperature as the calorimeter. This jacket consists of two nickel-plated brass cans, the smaller one (30.5 cm. high and 15.3 cm. in diameter) so fitting into the larger one (35 cm. high and 19 cm. in diameter) that there is an annular space about 17 mm. wide between the two cans. Two slits are cut in opposite sides of the outer can and two small brass tubes with corresponding slits are soldered to the can so as to provide on the one side, F, for the immersion of a Beckmann thermometer and on the other, G, for a turbine stirrer, H. This annular space, with its two cylindrical enlargements, is filled with about 3500 cc. of water. The water is heated or cooled to correspond with the temperature of the calorimeter water; to heat it, a Simplex electric heating coil (6.8 amp., 750 watts), helical in shape, which is immersed in the water, is used; for cooling, cold water from the city mains is admitted through a small pipe at the bottom of the outer can, the excess of water in the jacket passing out through an overflow. A 2° rise in temperature can be obtained in three minutes by passing the current through the heater for 50 seconds; the cooling is much more rapid.

The calorimeter is protected from exchange of heat at the top by means of a cover, which fits snugly in the top of the water jacket and reaches to 13 mm. from the top of the calorimeter can. This cover consists of two dead-air compartments, J and K, separated by an asbestos plate. The side of the lower dead-air compartment, K, is of metal to allow contact with the outer water jacket and so cause this compartment to take the temperature of the water jacket (and consequently that of the calorimeter) in preference to the temperature of the room air. The other parts of the cover are of non-conductible material—fiber and asbestos—, the top consisting of a larger sheet of fiber for convenience in handling. Soft rubber packing is on the bottom of the cover. Three hard rubber tubes pass through the cover, two for the stirrer rods and one for the thermometer, and the ignition wires pass through a small groove on one side.

Auxiliary Apparatus.—The cans are encased in a wooden box, which serves as a support and also protects them from undue local heating or cooling. A door in front opens to a pet-cock on the water jacket for emptying the latter if desired.

A motor, resting on a shelf back of the box, actuates the two stirrers. The outer stirrer is connected directly to the motor shaft by a cord, and rotates about 750 times a minute. The inner stirrer is raised and lowered 44 times per minute, a distance of 6.5 cm., by means of a worm gear fastened directly to the armature shaft of the motor. This worm gear is connected to the stirrer by a cord passing over pulleys on the back of the box to a cross bar with spring, L, which grips the tops of the stirrer rods.

The ignition of the substance in the bomb is accomplished by a 110-volt current passing through three 32 c. p. lamps in parallel; these lamps are placed in receptacles beneath the shelf upon which the motor rests. The wires are attached to the bomb before lowering it into place in the calorimeter, and later attached to a plug outside which connects it to the switch used for ignition; this avoids handling the wires under water after the bomb is immersed.

The electric switches have been placed on the front of the case. One controls the 110-volt circuit, and there is one each for the motor, the electric heater, and the ignition. Two push buttons for the thermometer tappers are also placed on the front of the case.

The thermometers are held by a special form of support, M, consisting of two brass tubes, one for each thermometer. Attached to the top of each thermometer is a collar with a handle, which fits into a slit in the wall of the tube support. When lowered, the collar handle rests on the bottom of the slit; when raised, the handle is turned 90° and thus rests in a notch in the top of the support. When the thermometers are not being used, the whole support is swung to one side out of the way; when they are to be used, the support is swung back into position and automatically centers itself so that both thermometers are directly above the corresponding openings in the cover. We have been using two Beckmann thermometers, readable to 0.001°, although a cheaper thermometer could doubtless be used for the water jacket. For tapping the thermometer, we use the hammer of a small electric bell, N, attached to the thermometer support.

Method of Making a Combustion.—In a combustion, the substance to be burned is prepared, weighed, and put in the bomb and the bomb charged to 25 atmospheres with oxygen. The calorimeter water is brought to a temperature of about 2° lower than that of the room, as it is generally planned to have a 2° rise in the combustion and it has been found advantageous to have the final temperature of the calorimeter about the same as the room temperature. The calorimeter water is then weighed. The system is assembled; the calorimeter can, with water and stirrer, is lowered into the jacket, and then the bomb, connected with the ignition wires, is in turn lowered into the calorimeter can; the cover is put in place, the thermometers adjusted, and the stirrers connected and started. By means of the electric heating coil and the cold water, the temperature of the water jacket is adjusted to about 0.1° lower than that of the calorimeter system and a temperature constant to within 0.001° is readily obtained in the calorimeter system for several minutes. It has been found that the water jacket should be slightly colder than the water in the calorimeter to compensate for the small amount of heat entering from the warmer room, probably through the tubes in the cover.

After the temperature of the calorimeter water has remained constant for several minutes, showing no interchange of heat, the switch for heating the water jacket is closed. The current is then passed through the heater for such a length of time as will be necessary to raise the outer water to the temperature it is expected the inner water will reach after the substance in the bomb is burned. The length of time required for this is calculated from the known fact that the heater gives a 1° rise for every 25 seconds the current is on. Forty-five seconds after the current is turned on, another reading of the calorimeter thermometer is taken, and the substance is ignited. The heating of the water jacket is begun before ignition, as the electric heater is somewhat sluggish. During the 45 seconds the current is on before ignition, the rise in temperature of the outer water indicates on the thermometer about 0.2°, showing that there is very little, if any, interchange of heat, but the rise of temperature becomes considerably more rapid after one minute, and the temperatures of the calorimeter and the water jacket are found to rise at about the same rate. After the ignition, the two thermometers are watched very carefully and if the temperature of the water jacket does not follow very closely the temperature of the calorimeter water, it is heated by the electric heater or cooled by cold water, as may be necessary to keep the two temperatures the same. Generally, however, little or no adjustment of the temperature of the outer water is necessary, as a careful timing of the heating of the jacket at the start will regulate the temperature. Readings of the thermometers are recorded every minute, and three or four minutes after ignition, the thermometer in the calorimeter water is found to attain a maximum reading which will remain constant practically as long as desired. The combustion now being completed, the thermometers are removed, the bomb opened and rinsed with water, and the rinsings titrated for nitric acid, using methyl orange as an indicator.

Calculation of Results.—The initial constant reading of the temperature of the calorimeter system subtracted from the final constant reading after the burning of the substance gives, after applying thermometer corrections, the total rise in temperature of the system. This rise multiplied by the weight of water (plus the hydrothermal equivalent of the apparatus) gives the total number of Calories liberated. From this is subtracted the heat resulting from the ignition (electrical energy and combustion of kindling material, such as cotton thread or iron wire) and from the formation of nitric acid. The result, divided by the weight of the substance, gives the number of Calories per gram of substance.

The water equivalent of the calorimeter system was determined by us by burning known amounts of cane sugar (rock candy), the heat of combustion of sugar being taken as 3957 Calories per gram.[1] The amount of water used in our calorimeter has, for convenience in calculating, been such that the weight of water plus the hydrothermal equivalent is equivalent to 2500 grams of water.

SPECIMEN COMBUSTION.

		Grams
Cane sugar:	Weight of substance taken..	1 2905
	Weight of water in calorimeter.......... ..	2125 8
	Hydrothermal equivalent.	374 2
		2500 0

Time.	Temperature of calorimeter water.	Temperature of water jacket.	
3.30	18.430°	18.36°	
3.31	18.430	18.38	
3.32	18.430	18.38	Electric heater on for 55 seconds at 3.32.15.
3.33	18.430	18.66	Ignition at 3.33.
3.34	19.200	19.60	
3.35	20.420	20.33	
3.36	20.478	20.45	
3.37	20.479	20.46	Room temperature, 20.7°.
3.38	20.479	20.49	

20.479°
—18.430

2.049°
Thermometer correction. +0.008 Ignition heat = 27.5 cal.
HNO_3 = 7.5 cal.

Total rise............. ..... 2.057°

2.057° × 2500 g. = 5143 cal.
5143 — 35 = 5108 cal.
5108 ÷ 1.2905 = 3958 cal. per gram.

---

[1] This value is that found by Fischer and Wrede, *Sitzungsberichte d. Koniglich. Preuss. Akad. d. Wissenschaften*, 5, 129 (January, 1908). If later investigation gives another more accurate result, the results obtained assuming 3957 as correct may be revised by proportion.

The apparatus here described has proved very efficient, and we are able to obtain very satisfactory duplicate results in two combustions of the same substance. Practically no trouble is experienced in obtaining a constant temperature of the calorimeter system either at the beginning or end of a combustion; in fact, with the room temperature even 5° higher than that of the calorimeter water, constant readings have been obtained. With this calorimeter, the time required for a combustion is much less than usual, inasmuch as long preliminary and final periods are avoided and the calculation is materially simplified.

NUTRITION LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON,
BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

A SIMPLE SYSTEM OF THERMODYNAMIC CHEMISTRY BASED UPON A MODIFICATION OF THE METHOD OF CARNOT.

BY EDWARD W. WASHBURN.

Received January 19, 1910

CONTENTS.

1. Introduction. 2. Description of the perfect thermodynamic engine. 3. The vapor pressure of a pure substance 4. The homogeneous physical mixture. 5. Homogeneous chemical equilibrium. 6. Heterogeneous chemical equilibrium. 7. Electromotive force 8. The colligative properties of a solution. 9. Summary and conclusion.

1. Introduction.

In order to determine the maximum amount of work which can be obtained from a given amount of heat by a fall in temperature, Carnot, in 1824, performed an "imaginary experiment," the Carnot Cycle. In performing this "experiment" Carnot made use of the simplest and most familiar example of a mechanism for obtaining work from heat, the cylinder and piston of the steam engine. He realized clearly that in order to obtain the desired relation he had only to *imagine* a mechanism which could operate under the most ideal conditions, one which represented the limit approached by all actual machines of the same class, as the losses due to friction, heat radiation and conduction, incomplete external compensation, etc., became indefinitely small. The reversible cyclical process thus invented by Carnot and later slightly modified by the work of Clapeyron and of Clausius, constitutes to-day the basis for the derivation of the mathematical formulation of the Second Law of Thermodynamics. Resting upon this law, the whole structure of thermodynamics has since been built up.

In the process of constructing our systems of thermodynamic chemistry, two general methods may be distinguished. The first of these, the analytic method, starts with Clausius' formulation of the Second Law in terms of entropy. The manner in which the entropy function might be used with advantage by the chemist was first illustrated by Horstmann, who applied it to many problems in chemical equilibrium. The later advocates of the analytic method, however, have not found it convenient to restrict themselves to the entropy function, but have defined and made use of a number of other thermodynamic functions. Willard Gibbs, in his masterly contributions to thermodynamic chemistry, defined four of these functions, his ε, ψ, χ and ζ functions; the ζ function, or the so-called Gibbs thermodynamic potential, being the one most commonly employed to-day. The system invented by Gibbs has been followed by Duhem, Planck, van der Waals, van Laar, and others, usually however receiving some modification at the hands of each investigator. Thus Planck, instead of using Gibbs' Zeta function, prefers another potential which he defines as equal to $-\zeta/T$, where T is the absolute temperature; and recently G. N. Lewis has constructed a very simple analytic system of thermodynamic chemistry by introducing two new functions, the fugacity, Ψ, and the activity, ξ, which are connected with each other by the equation, $\Psi = \xi RT$, and whose relation to Gibbs' Zeta function is expressed by the equation $\zeta = RT \ln \Psi + f(T)$. Although here classed among the analytic methods, this system owes a large part of its increased simplicity to the fact that its fundamental equations are derived by employing the second general method instead of starting with the entropy function as might have been done.

The second general method of constructing a system of thermodynamic chemistry is the Carnot method, or, as it is usually called to-day, the cyclical process method. This has been the favorite method among chemists, and to it we owe most of our advances in this branch of chemistry, as illustrated by the work of such men as van't Hoff, Ostwald, Arrhenius and Nernst. It is the simplicity of the processes involved in this method and the consequent protection against error which constitute its great advantages over the more intricate and abstruse, but yet not necessarily more rigorous methods based upon the entropy and thermodynamic potential functions. This has been well stated by Mach in his comment upon the discoverer of the second law: "Carnot, by whose ideas the whole of thermodynamics is ruled to-day, ... affords us the most pleasing picture of a genius who, without apparent exertion and without the labored application of intricate and cumbersome scientific methods, but solely through the consideration of the simplest processes, is able, almost without effort, to perceive the most fundamental truths."

The cyclical process method of deriving thermodynamic equations as applied by many of its advocates has been the subject of considerable adverse criticism mainly upon two grounds: (1) As usually carried out, the cyclical process consists of a series of steps, usually four, in each of which certain amounts of work and of heat are involved, the desired result being obtained by combining properly all the work and heat terms of the various steps in the cycle. The complete process is consequently rather long in some instances and is regarded by some writers as very cumbersome compared with some of the corresponding analytic methods. (2) In writing down the work and heat terms for the various steps of the cycle, it is customary to introduce some assumption such as the perfect gas law or one of the laws of dilute solutions, with the result that a rigorous, purely thermodynamic equation is not obtained, but only an approximate one containing one or more arbitrary assumptions. The possibility of introducing these assumptions is the most serious objection which can be offered to the cyclical process method, as carried out at present. So general is this practice, that in the text-books employing this method one looks almost in vain for exact thermodynamic equations such as those relating to chemical equilibrium, for example.

In the following pages a modification of the Carnot method will be described which eliminates completely both of these objections: (1) the cycle is reduced to a single step and the desired relation can be written down simply by inspection; (2) the differential equation so obtained will always be entirely rigorous because it is impossible to introduce into the process any assumptions except the Second Law of Thermodynamics. This gain in simplicity and exactness is accomplished by joining together the various pistons of the ordinary cycle so as to form a single complete engine which we shall call the Perfect Thermodynamic Engine. After describing the construction and operation of this engine, its application will be illustrated by using it in order to derive a number of the more important relations of thermodynamic chemistry. While the treatment of the subject in the following pages must necessarily be rather concise, it can, I believe, be followed easily by any chemist familiar with the elements of thermodynamics and the calculus.

2. The Perfect Thermodynamic Engine.

Figures 1, 2 and 3 illustrate different types of the engine, the essential parts of which are the following (see Fig. 1):

Two *reaction chambers* (**E** and **E′**) contain the system under consideration. Each chamber is placed in a *reservoir* (**R** and **R′**) of infinite heat capacity for the purpose of maintaining a constant temperature within the chamber. Each chamber is fitted with a set of *cylinders* (**A, B, D, A,′ B′, D′**, etc.) which connect with it through suitable *semipermeable membranes*, **aa, a′a′**. The cylinders are fitted with frictionless pistons (**A, B, D, A′, B′, D′**, etc.), some of which are semipermeable, others impermeable. Each corresponding pair of pistons is connected by a rigid piston rod, thus forming a *compound piston* (**AA′, BB′, DD′**, etc.). The piston rods have zero heat capacities and are non-conductors of heat and electricity, and the two reservoirs, **R** and **R′**, are otherwise insulated from each other so that no irreversible transfer of heat can take place between them. During the *operation* of the engine the following conditions must be fulfilled: (1) The two reservoirs must never differ from each other, in temperature, by more than an infinitesimal amount; when such a difference exists, the temperature of **R** will be designated by T and that of **R′** by $T + dT$; (2) The pressure difference against the two heads of a compound piston must never exceed an infinitesimal amount; the pressures exerted against the pistons of **E** will be designated by p, P, etc., those exerted against the pistons of **E′**, by $p + dp$, $P + dP$, etc. The *operation* of the engine consists in the movement of the com-

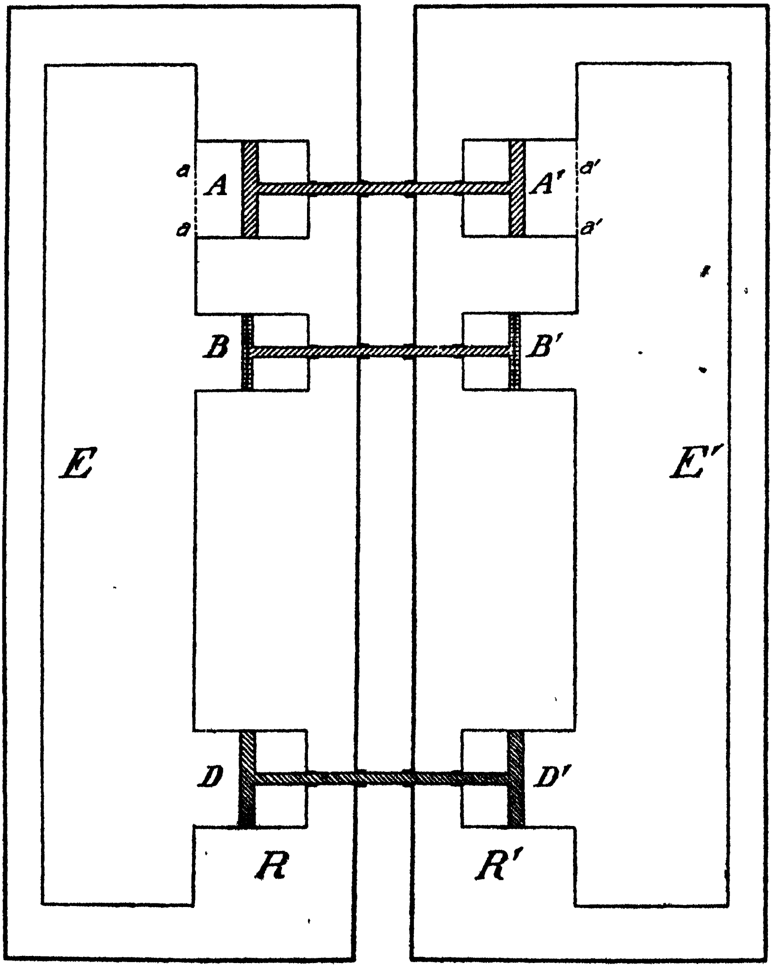


Fig. 1.

pound pistons through finite distances, accompanied by corresponding processes which take place within the reaction chambers. Other conditions which must be fulfilled during this operation are (3) that each compound piston must always move so as to produce the maximum amount of external work, there being applied to it a compensating external pressure substantially equal to the pressure difference on the two piston-heads; and (4) that the rates of motion of all the pistons must be so regulated that the equilibrium within the reaction chambers remains undisturbed. In other words, the engine must operate reversibly.

By the Second Law of Thermodynamics, the following two theorems, regarding the work produced during the *operation* of the engine, are true:

Theorem I.—The total work produced during the isothermal *operation* (temperature of **R** = temperature of **R**′) of the engine is equal to zero.

Theorem II.—When the engine operates as a heat engine (temperature of **R** = T, that of **R**′ = $T + dT$), the total work produced is equal to $Q\ dT/T$, where Q is the heat absorbed from reservoir **R**′.

It should also be noted that the algebraic expression for the work produced by any compound piston during the operation of the engine will have a positive sign when the motion is from right to left and a negative sign when the motion is from left to right. Since one complete "operation" of the engine, as we shall use the term, is not a complete cycle, it will be necessary to demonstrate the truth of these two theorems. This will be done in the next section, in which certain other details concerning the construction and operation of the engine will also be described.

3. The Vapor Pressure of a Pure Substance.

The equilibrium between vapor and liquid (or vapor and solid) in a one-component system may be altered: (1) by changing the total pressure on the liquid (or solid) phase at constant temperature; (2) by changing the temperature of the system while keeping the pressure on the liquid (or solid) phase constant; or (3) by changing the temperature of the system and at the same time allowing the total pressure on the liquid (or solid) phase to vary in such a manner that it is always equal to the vapor pressure. We shall make use of the perfect thermodynamic engine in order to determine the separate effects of these different factors upon the vapor pressure of a pure liquid. The treatment for the case of a pure solid is perfectly analogous.

The Pressure Coefficient (T = *const.*).—We shall use the engine shown in Fig. 1, omitting, however, pistons and cylinders **BB**′. The arrangement of the engine is as follows:

Chamber E: Filled with the liquid whose vapor-pressure, acting through the membrane **aa** (permeable to vapor only) against piston **A**, is p. Total pressure on liquid, acting against piston **D**, is P. Temperature of **R** = T.

Chamber **E′**: Exactly as **E** except that the total pressure on the liquid, acting against piston **D′**, is $P + dP$ and the vapor-pressure, acting against piston **A′**, is $p + dp$.

To operate the engine allow piston **AA′** to move reversibly toward the left until one mol of the vapor in cylinder **A** condenses through the membrane into chamber **E** and an equal volume v is evaporated from chamber **E′** into cylinder **A′**. At the same time and at such a rate as not to disturb the equilibrium in either chamber, piston **DD′** moves reversibly toward the right through the volume V occupied by one mol of the liquid under the pressure P. The work done by piston **AA′** is vdp, and that done by piston **DD′** is $-VdP$. By the Second Law (*i. e.*, Theorem I) the total work is equal to zero, which gives us the equation

$$vdp - VdP = 0 \qquad (1)$$

or

$$(\partial p/\partial P)_T = V/v, \qquad (2)$$

an equation first obtained by Poynting.[1]

If the vapor obeys the perfect gas laws, equation (2) assumes the form

$$(\partial \ln p/\partial P)_T = V_0(1-\alpha P)/RT \qquad (3)$$

where V_0 is the molecular volume of the liquid under zero pressure and α is the mean coefficient of compressibility of the liquid as defined by the equation, $\alpha = (V_0 - V)/V_0P$. The equation can now be integrated. Since the right-hand member of equation (2) is necessarily positive, the vapor pressure always increases with increase in pressure on the liquid phase. The coefficient, $(\partial p/\partial P)_T$, is small for temperatures considerably removed from the critical temperature (thus for water at 0°, $(\partial p/\partial P)_{T=273°} = 3.6 \cdot 10^{-6}$ mm. per atmosphere) but increases with the temperature and becomes equal to 1 at the critical temperature.

Proof of Theorem I.—We have assumed Theorem I in writing equation (1). In order to demonstrate the truth of this theorem for the present case, it is only necessary to show that the engine can be restored to its original condition without leaving any residual effect in the surroundings. Turning, therefore, to our engine after the completion of the operation, we notice that as regards the vapor, the final state of the system differs from its original state in that we have (in cylinder **A′**) $1 + dx$ mols of vapor occupying the volume v under the pressure $p + dp$ instead of having (in cylinder **A**) 1 mol of vapor occupying the volume v under the pressure p. This means that while only one mol of liquid has been produced in chamber **E**, $1 + dx$ mols of liquid have been evaporated from chamber **E′**, dx being obviously expressed by the relation $dx = (\partial x/\partial p)_{v,T}dp$. But the removal of this dx mol of liquid from chamber **E′** would, unless compensated in some manner, cause a corresponding change in the total pressure in this chamber, because it will be remembered that during the operation of the engine, piston head **D**$'$ moves toward the right simply through the volume V of one mol of liquid under pressure P, not through the volume of $1 + dx$ mols of liquid under the pressure $P + dP$. To avoid this pressure change a little device, **X** (not shown in Fig. 1, but shown in Fig. 1*a*), acts automatically during the operation of the engine to maintain a constant pressure in chamber **E**$'$. This device applies the constant pressure $P + dP$ to a little auxiliary piston, π', which, during the operation of the engine, gradually introduces reversibly into chamber **E**$'$, such an amount, dx' mol, of liquid as suffices to maintain the constant pressure $P + dP$ within this chamber. During this process (which we need not consider as a part of the "operation" of the engine for reasons stated below) the device **X** gives out the energy $(P + dP)dV'$.

---

[1] Poynting, *Phil. Mag.* [5], 12, 32 (1881).

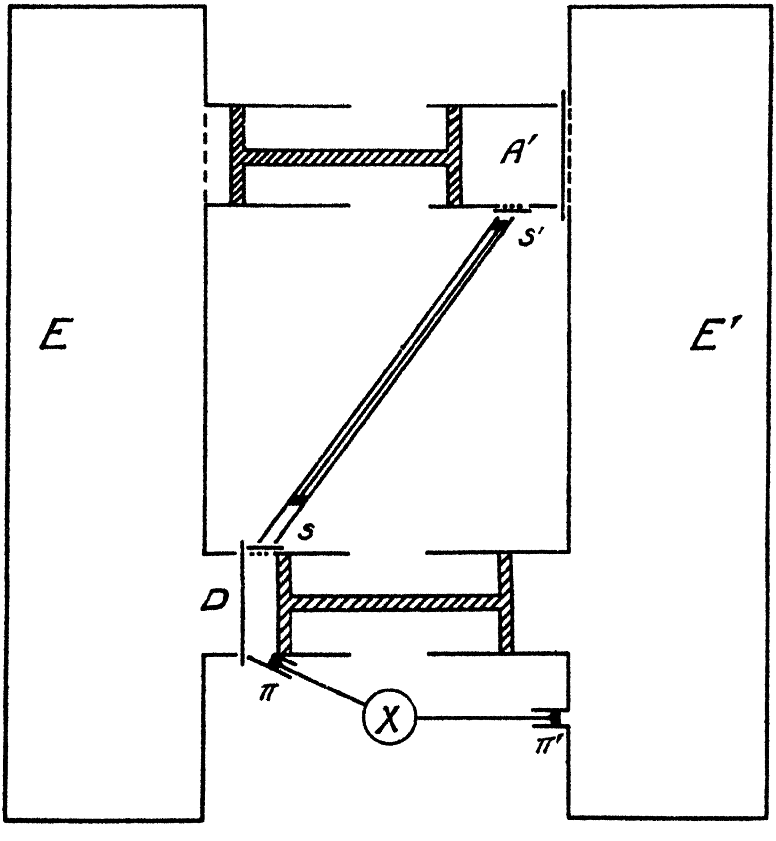


Fig. 1*a*.

As soon as the "operation" of the engine has been completed, another automatic device (shown in Fig. 1*a*) immediately acts to restore the system to its original condition. This device is the little compound piston **ss′**. The head **s′** rests against a slider which separates it from cylinder **A′** and which at the conclusion of the "operation" of the engine slides back so that the vapor pressure $p \pm dp$ acts against the piston head **s′**. Below the piston head **s** is contained dx mol of vapor at the pressure p separated from cylinder **D** by a semipermeable membrane and by an impermeable slider which on sliding back puts the dx mol of vapor into communication with the liquid in cylinder **D**, with which it is in equilibrium. The action of this device is as follows· When the "operation" of the engine has been completed the one mol of liquid in cylinder **D** and the $1 + dx$ mols of vapor in cylinder **A′** are automatically cut off from the rest of the engine (as shown in Fig. 1*a*), the little sliders at **s** and **s′** move back and piston **ss′** moves downward drawing dx mol of vapor out of cylinder **A′** (the pressure consequently dropping to p) and condensing it as liquid into the one mol of liquid in cylinder **D**, whose pressure thereby is raised to $P + dP$. *At the same time*[2] the little piston, π, which is attached to the device **X** moves downward through the volume dV'. The system is now in its original condition, *i. e.*, we have 1 mol of vapor under the pressure p and $1 + dx'$ mols of liquid under the pressure $P + dP$, which was the condition of the system before the operation of the engine.

Let us consider the work produced by the action of these various automatic devices which serve to restore the system to its original condition. The piston **ss′** moves through the volume dv under the pressure dp and therefore performs the work $dp\,dv$, which is a differential of the second order and consequently negligible. During the movement of the little piston π the device **X** takes up the energy $(P + dP)dV'$. But this is the same amount of energy which it gave out previously to piston π'. The operation of the device **X**, therefore, involves no work. The total work involved in restoring the system to its original condition, after an "operation" of the engine, is therefore made up of differentials of a higher order than the first and is consequently entirely negligible in comparison with the work performed during the "operation" itself. Although we have shown this to be true only for the simple case just considered, it is clear that it must also be true for any engine of this type, in which the intensity factor of some form of energy is different in the two chambers because of a difference dP in the total pressures on the chambers, and whose operation consists in removing one or more substances from one chamber and forcing them into the other by means of compound pistons moving in a manner analogous to the simple case just considered. *Theorem* I *is therefore true.*

---

[2] Strictly speaking, the movement of piston π should not begin until such a portion of the dx mol has been forced into D, as suffices to raise its pressure to $P + dP$.

The Temperature Coefficient (*P = const.*).—Let us now consider the effect of temperature changes upon the vapor pressure of a liquid which is under constant external pressure P, such changes as would occur for example on heating the liquid in an open vessel exposed to the atmospheric pressure. As in the previous case, we will make use of the engine shown in Fig. 1, omitting cylinder **BB′** The arrangement is as folllows:

Chamber **E**: Filled with the liquid whose vapor pressure acting through the semipermeable (*i. e.*, only to the vapor) membrane against piston **A** is p. Total pressure on liquid, acting against piston **D**, is P. Temperature of **R** $= T$.

Chamber **E′**: Exactly as **E** except that the temperature of **R′** is $T + dT$ and the vapor pressure, acting against piston **A′**, is $p + dp$.

The operation of the engine is the same as in the preceding case. Piston **AA′** moves reversibly toward the left under the pressure dp, until 1 mol of the vapor in cylinder **A** is condensed into **E** and an equal volume evaporated from **E′** into cylinder **A′**. Piston **DD′** moves toward the right, under zero pressure, through the volume V occupied by one mol of the liquid, in **E**. The work done by piston **AA′** is vdp, that done by piston **DD′** is zero. We have, therefore, by the Second Law (*i. e.*, *Theorem* II),

$$vdp = L_p dT/T \tag{4}$$

or

$$(\partial p/\partial T)_P = L_p/vT, \tag{5}$$

an equation previously obtained by Lewis[3]

L_p, the heat absorbed from reservoir **R′**, is the molecular heat of vaporization of the liquid under constant pressure. Since this is a positive quantity, the vapor pressure always increases with rise in temperature. If the vapor behaves as a perfect gas, we can put $v = RT/p$ in equation (5), which gives us

$$(\partial \ln p/\partial T)_P = L_p/RT^2. \tag{6}$$

To integrate, it is only necessary to express L_p as a function of T, which can be readily done by means of the thermodynamic relation,

$$\partial L_p/\partial T = c_p - C_p, \tag{7}$$

where c_p and C_p are the molecular heat capacities of vapor and liquid respectively, under constant pressure.[4]

Proof of Theorem II.—Let us now return to our engine and compare its final state with its initial state. As regards the vapor we have (in

---

[3] *Proc. Amer. Acad.*, 37, 53 (1901); *Z. physik. Chem.*, 38, 205 (1901).

[4] Equation 7 also contains the assumption that the vapor behaves as a perfect gas. The purely thermodynamic equation for the temperature coefficient of L_p is

$$(\partial L_p/\partial T)_P = c_p - C_p + L_p/T - (L_p/v)(\partial v/\partial T)_p. \tag{7a}$$

cylinder **A′**) 1 + dx mols of vapor occupying the volume v at the temperature $T + dT$ and pressure $p + dp$ instead of having (in cylinder **A**) 1 mol of vapor at the temperature T and pressure p. dx is defined by the equation $dx = (\partial x/\partial p)_{v,T}(\partial p/\partial T)_p dT + (\partial x/\partial T)_{v,p} dT$, and may, in general, be either positive or negative since the second term of this expression is essentially negative. 1 + dx mols of liquid have consequently evaporated from chamber **E′** during the operation and in order to prevent a consequent change in pressure in this chamber, the automatic device **X** acts just as in the preceding case to introduce dx mol of liquid into **E′**, replacing that which evaporates into cylinder **A′**, and thereby performs the work PdV.

At the completion of the operation of the engine, the 1 + dx mols of vapor are cut off from cylinder **A′** and brought into reservoir **R**, whereupon the temperature returns to T. By means of the piston **ss′** (Fig. 1*a*) dx mol is then removed from it (its pressure thereupon falling to p) and condensed into the 1 mol of liquid which has been cut off from chamber **E** and whose pressure is thereby raised to $P + dP$. The work involved in this operation is that done by piston **ss′**, which is $dp\,dv$. The one mol of liquid is now brought into reservoir **R′** (whereupon its temperature returns to $T + dT$) and is connected to the device **X**, which removes dx mol from it, its pressure thereby falling to P. The whole system is now in its original condition. The work absorbed by the device **X** in this last step is $P\,dV$, the same amount which it previously gave out. Therefore the restoration of the system to its original condition after the operation of the engine does not leave any residual effects in the surroundings as far as work is concerned. As regards the heat absorbed from reservoir **R′** during the restoration, it is clear that since the temperature change is infinitesimal, the heat absorbed must be a differential quantity and consequently negligible in comparison with the finite amount of heat L_p absorbed during the operation of the engine. *Theorem* II *is therefore true.*

These two examples suffice to show that the restoration of the system to its original condition after the operation of the engine involves no work or heat terms which need to be considered. The whole effective work of the process is therefore performed entirely by the compound pistons of the engine and we may therefore, in the future, confine our consideration solely to these pistons and apply Theorems I and II directly to them. The various automatic devices which have been described for restoring the system to its original condition are understood to be a part of every engine, but since their action does not involve any work it will not be necessary to pay any attention to them in the future.

The Temperature Coefficient ($P = p$).—The latent heat of vaporization of a liquid is usually determined by condensing (in a calorimeter) the vapor of the boiling liquid. Under these conditions the liquid always vaporizes, not under constant pressure at all temperatures, but under its own vapor pressure at each temperature. The temperature coefficient of the vapor pressure under these conditions can be at once written down, by using the engine shown in Fig. 1. The arrangement is exactly as in the preceding case except that the pressure against piston **D** is p and that against piston **D′** is $p + dp$. The operation is the same as before and we obtain at once the relation

$$vdp - Vdp = L_p dT/T \tag{8}$$

or

$$(\partial p/\partial T)_{P=p} = L_p/(v-V)T \tag{9}$$

which is the familiar Clausius-Clapeyron equation.

L_P and L_p, the latent heats of vaporization of a liquid under the pressure P, and under its own vapor pressure, p, respectively, will not differ much unless the difference between P and p is large or the difference between v and V is small. In the case of water, for example, if $P = 1$ atmosphere, the difference between L_P and L_p could never exceed 0.005 per cent. L_p is the one which is usually determined experimentally, but A. W. Smith[1] has recently made a very accurate determination of L_P by bubbling air through water, the temperature of which was kept constant by electrical heating.

Solid-liquid Equilibrium. By filling the chambers of the engine with a pure solid and the cylinders with the pure liquid in equilibrium with it, we can study the effects of temperature and pressure upon such a system, in exactly the same way as for the liquid-gas or solid gas equilibrium described above, the equations obtained being identical in form with those just derived

4. The Homogeneous Physical Mixture.

In this section we shall make use of the perfect thermodynamic engine in deriving the equations expressing the effects of pressure, composition and temperature upon the partial vapor pressures and the osmotic pressures for any homogeneous physical mixture. Before taking up the derivations, however, it will be necessary to define accurately the term "osmotic pressure" as we shall use it.

Consider any homogeneous liquid mixture of n components (A, B, C, etc.) under the external pressure P. Let us take any one of the components, A for example, in the pure liquid state and subject it to such an external pressure P_A that its vapor pressure shall be equal to its partial vapor pressure from the mixture. If now the pure liquid A be placed in communication with the mixture through a membrane permeable only to A, the system will be in equilibrium as respects the passage of A into or out of the mixture. The difference between the pressures P_A and P is called the "osmotic pressure." For the simplest type of mixture it depends only upon the specific volume and compressibility of the pure substance A and upon its mol fraction in the mixture, for a given value of T and P. It would seem preferable therefore to speak of this pressure difference as the "osmotic pressure" of the substance A, since it is essentially determined by the properties of this substance. Principally on account of historical reasons, however, it is customary to speak of this pressure difference as the "osmotic pressures" of all the other components of the mixture except the substance A. In what follows it is essential that this pressure difference shall be referred directly to the substance which is present in the pure liquid state, and we will therefore speak of it as "the osmotic pressure referred to A as the solvent" or, briefly, as "the osmotic pressure referred to A." *In any homogeneous (gaseous, liquid or solid) mixture, therefore, the osmotic pressure* Π_A *referred to any constituent,* A, *is defined by the equation,* $\Pi_A = P - P_A$, *where* P *is the external pressure on the mixture and* P_A *is the external pressure on the pure substance* A *(in the same state of aggregation) when it is in equilibrium with the mixture through a membrane permeable only to itself.*[6]

---

[1] *Phys. Rev.*, 25, 145 (1907).

The following treatment, together with the equations obtained, is equally applicable to a solid, liquid or gaseous homogeneous, physical mixture of any number of components, but in developing our equations we shall find it convenient to fix our attention upon a homogeneous liquid mixture of say four components. The composition of the mixture is expressed by the equation $N_A + N_B + N_M + N_N = 1$, where N_X represents the mol fraction of any constituent X. The mol fraction of any constituent (A, for example) is defined by the equation $N_A = n_A/(n_A + n_B + n_M + n_N)$, where n_A, n_B, etc., represent the number of mols of the various constituents in any given quantity of the mixture.

The Pressure Coefficient (N, T = *const.*).—1. Vapor Pressures: Using the engine shown in Fig. 2, the arrangement is as follows (Temperature of **R** = temperature of **R′** = T):

Chamber **E**: Filled with the liquid mixture under the total pressure P applied by means of piston **D**. The partial vapor pressures of the various constituents (each acting through a membrane permeable only to its own vapor), are, p_A acting against piston **A**, p_B against **B**, p_M against **M**, and p_N against **N**.

Chamber **E′**: Filled with the liquid mixture under the total pressure $P + dP$ applied by piston **D′**, the partial vapor pressures being $p_A + dp_A$ acting against piston **A′**, $p_B + dp_B$ against **B′**, $p_M + dp_M$ against **M′** and $p_N + dp_N$ against **N′**.

[6] This definition is essentially the same as that given by A. A. Noyes (*Z. physik. Chem.*, 35, 707 (1900)). Its advantages over the more common one will become evident as we proceed.

At the beginning of the operation each of the four vapor pistons is at the right-hand end of its stroke, so that piston heads **A′**, **B′**, **M′**, and **N′** are in contact with the semipermeable membranes separating the cylinders from **E′**. The operation of the engine consists in the simultaneous movement of all four vapor pistons toward the left until 1 mol of the mixture has been evaporated from **E′** and condensed into **E**. At the same time piston **DD′** moves toward the right through the volume $(\Sigma\overline{V})$ of one mol of the liquid mixture. By the Second Law (Theorem I) the total work is equal to zero, giving us the equation,

$$N_A v_A dp_A + N_B v_B dp_B + N_M v_M dp_M + N_N v_N dp_N - (\Sigma\overline{V})dP = 0 \quad (10)$$

or

$$(N_A v_A \partial p_A + N_B v_B \partial p_B + N_M v_M \partial p_M + N_N v_N \partial p_N/\partial P)_{N,T} = (\Sigma\overline{V}) \quad (11)$$

which for brevity we shall write in the form

$$[(\Sigma N_A v_A \partial p_A)/\partial P]_{N,T} = (\Sigma\overline{V}) \quad (12)$$

In these equations V_x is the volume of one mol of the substance X in the vapor state under the pressure p_x.

2. Osmotic Pressures: If the cylinders contain the pure components in the liquid state instead of the gaseous state the respective partial pressures are osmotic pressures instead of vapor pressures, and allowing the engine to operate as before, we can write down at once the equation

$$[(\Sigma N_A V_A \partial \Pi_A)/\partial P]_{N,T} = (\Sigma N\overline{V}) \quad (13)$$

in which V_A, V_B, etc., represent the molecular volumes of the pure substances A, B, etc., in the liquid state under the pressures $P - \Pi_A$, $P - \Pi_B$, etc., respectively.[7]

The Composition Coefficient (P, T = const.).—1. Vapor Pressures: We shall now proceed to determine the effect of a slight change in the composition of a mixture, upon the partial vapor pressures of its constituents. Let us change the mol fraction of constituent A, for example, from N_A to $N_A + dN_A$. The arrangement of the engine is exactly as in the preceding except that the total pressure acting against **D** and **D′** is P for both chambers, the dp differences in the partial vapor pressures being due to the fact that the composition of the mixture in chamber **E′** has been altered by the addition of dN_A mols. of A. The operation of the engine is exactly as above and we have by the Second Law (Theorem I),

---

[7] The expression $(\Sigma N\overline{V})$ is used to represent the volume of one mol of the mixture because this volume may be regarded as equal to the sum of the partial volumes of the components as expressed by the equation $N_A\overline{V}_A + N_B\overline{V}_B + N_M\overline{V}_M + N_N\overline{V}_N = \Sigma N\overline{V}$, in which $\overline{V}_A$, $\overline{V}_B$, etc., represent the *partial* molecular volumes of the respective constituents in the mixture. The partial molecular volume of any constituent is equal to the increase in the volume of an infinite amount of the mixture when one mol of the constituent is added to it. Similar relations may be stated for the quantities $(\Sigma N\overline{L})$ and $(\Sigma N\overline{D})$ which appear in equations (18) and (19).

$$N_{\mathrm{A}}v_{\mathrm{A}}dp_{\mathrm{A}} + N_{\mathrm{B}}v_{\mathrm{B}}dp_{\mathrm{B}} + N_{\mathrm{M}}v_{\mathrm{M}}dp_{\mathrm{M}} + N_{\mathrm{N}}v_{\mathrm{N}}dp_{\mathrm{N}} = 0, \tag{14}$$

or

$$[(\Sigma N_{\mathrm{A}}v_{\mathrm{A}}\partial p_{\mathrm{A}})/\partial N_{\mathrm{A}}]_{P,T} = 0. \tag{15}$$

2. Osmotic Pressures: As in the preceding case, if the cylinders contain the pure liquid components the operation of the engine gives us the equation

$$-[(\Sigma N_{\mathrm{A}}V_{\mathrm{A}}\partial \Pi_{\mathrm{A}})/\partial N_{\mathrm{A}}]_{P,T} = 0. \tag{16}$$

The Temperature Coefficient (*P*, *N* = *const.*).—1. Vapor Pressures: The arrangement and operation of the engine is exactly the same as in the preceding case except that the composition is identical in both chambers and the temperature of **R** = T and that of **R′** = $T + dT$. The Second Law (Theorem II) gives us at once the relation

$$N_{\mathrm{A}}v_{\mathrm{A}}dp_{\mathrm{A}} + N_{\mathrm{B}}v_{\mathrm{B}}dp_{\mathrm{B}} + N_{\mathrm{M}}v_{\mathrm{M}}dp_{\mathrm{M}} + N_{\mathrm{N}}v_{\mathrm{N}}dp_{\mathrm{N}} = (\Sigma NL)dT/T \tag{17}$$

or

$$[(\Sigma N_{\mathrm{A}}v_{\mathrm{A}}\partial p_{\mathrm{A}})/\partial T]_{P,N} = (\Sigma NL)/T \tag{18}$$

where (ΣNL) is the latent heat of vaporization of one mol of the mixture at constant pressure and composition.[7]

2. Osmotic Pressures: With the pure liquids in the cylinders we obtain the equation

$$-[(\Sigma N_{\mathrm{A}}V_{\mathrm{A}}\partial \Pi_{\mathrm{A}})/\partial T]_{P,N} = (\Sigma N\bar{D})/T \tag{19}$$

where $(\Sigma N\bar{D})$ is the latent heat of separation of one mol of the mixture into its pure liquid components under equilibrium conditions. Its exact meaning is clearly evident from the operation of the engine.[7]

Discussion.—The equations which we have just derived involve nothing but the two laws of thermodynamics and they contain all th [illegible] formation which thermodynamics alone is capable of yielding r [illegible] the relations existing among the partial vapor pressures or osm [illegible] sures for a homogeneous mixture. We shall not, in the pres [illegible] discuss these important equations further, although many in [illegible] examples of their transformations and applications in special cases present themselves. It will be sufficient to note here that if the vapors behave as perfect gases, the vapor pressure equations assume the forms

$$[(\Sigma N_{\mathrm{A}}\partial \ln p_{\mathrm{A}})/\partial P]_{N,T} = (\Sigma NV)/RT, \tag{20}$$

$$[(\Sigma N_{\mathrm{A}}\partial \ln p_{\mathrm{A}})/\partial N_{x}]_{P,T} = 0, \tag{21}$$

and

$$[(\Sigma N_{\mathrm{A}}\partial \ln p_{\mathrm{A}})/\partial T]_{N,P} = (\Sigma N\bar{L})/RT^{2}. \tag{22}$$

The equation of Duhem-Margules for the partial vapor pressures of a binary mixture is a form of equation (21). It will also be noticed that the equations derived in section (1) for a pure substance are special forms of these equations for a one-component system.

By making the two chambers of our engine infinite in volume and removing only one constituent we can obtain the following equations for the partial vapor pressure or osmotic pressure referred to *one constituent alone.*

$$(\partial p_A/\partial P)_{N,T} = V_A/v_A. \quad (23) \qquad (\partial \Pi_A/\partial P)_{V,T} = -\bar{V}_A/V_A. \quad (23a)$$

$$(\partial p_A/\partial T)_{N,P} = L_A/v_A T \quad (24) \qquad (\partial \Pi_A/\partial T)_{N,P} = -\bar{D}_A/V_A T. \quad (24a)$$

The absence of an equation for one constituent, corresponding to equation (15), will be noticed. Thermodynamics is incapable of yielding any information concerning the changes in the partial vapor pressure (or osmotic pressure) of one constituent of a mixture, with a change in the composition of the mixture, other than the information contained in equation (15).

Since $\bar{V}_A$ may be either positive or negative,[7] the partial vapor pressure of a constituent of a mixture, unlike the vapor pressure of a pure substance (see page 472), may be in some cases increased and in others decreased by increasing the total pressure on the mixture. L_A, the partial molecular heat of vaporization of any constituent, A, is the heat absorbed when one mol of A is vaporized reversibly from an infinite amount of the mixture. If the vapor obeys the perfect gas laws equation (24) becomes

$$(\partial \ln p_A/\partial T)_{N,P} = (L_A - D_A)/RT^2, \qquad (25)$$

where L_A is the molecular heat of vaporization of the *pure liquid* A, and D_A is the heat *absorbed* when one mol of liquid A is mixed with an infinite amount of the mixture. $-D_A$ is obviously the ordinary molecular *heat of dilution* of a solution with one of its components, A. The equation now contains only quantities which can be readily measured.

In a similar way equation (24*a*) for the *temperature coefficient of osmotic pressure* can be put in a more practical form if we replace $\bar{D}_A$ by $(D_A - \Pi_A V_A)$, which is equal to it by the First Law. If we choose to refer the heat of dilution to *unit volume* of solvent instead of to one mol we have[8] $q = D_A/V_A$ and equation (24*a*) assumes the familiar form of the Helmholtz equation

$$(\partial \Pi_A/\partial T)_{P,N} = (\Pi - q)/T. \qquad (26)$$

5. Chemical Equilibrium: A. Homogeneous.

Let us consider any chemical equilibrium, expressed by the equation

$$a\text{A} + b\text{B} + \ldots \rightleftarrows m\text{M} + n\text{N} + \ldots \qquad (27)$$

in which *a* mols of the substance A react with *b* mols of the substance B, etc., to form *m* mols of the substance M and *n* mols of the substance N, etc. The substances entering into the reaction are in equilibrium with each other in any homogeneous phase and there may or may not also be present in the phase one or more other substances which do not take part in the reaction: a solvent or an indifferent gas, for example. As in the preceding section the composition of the phase is represented by the equation

$$N_A + N_B + \ldots + N_M + N_N + \ldots + N_1 + N_2 + \ldots = 1 \quad (28)$$

where N_X is the mol fraction of the constituent X, numercial subscripts referring to substances which do not take part in the chemical equilibrium.

Our problem is to determine in what direction and to what extent the chemical equilibrium is displaced by, (1) increasing the concentration (*i. e.*, the mol fraction) of one of the reacting substances, (2) increasing the total pressure on the phase, and (3) increasing the temperature of the system. In deriving our fundamental equations, it will be simpler to fix our attention chiefly upon some particular phase, and we shall choose a gaseous phase, which, in addition to the reacting substances, contains also an indifferent gas which we shall call constituent, 1. It would correspond to a solvent if we were dealing with a liquid or solid solution.

[The treatment of chemical equilibrium in a homogeneous liquid or solid phase is quite analogous, it being simply necessary to replace partial gas pressure p_X by the osmotic pressure Π_X. It will be sufficient, therefore, in the following treatment, to indicate parenthetically (in brackets) the necessary changes in the process and the corresponding equations for these cases.]

Arrangement of the Engine.—We shall make use of the engine shown in Fig. 2. The arrangement is as follows:

Chamber **E**: Filled with the gaseous mixture as described above, the composition of the mixture being represented by the equation

$$N_A + N_B + \ldots + N_M + N_N + \ldots + N_1 = 1.$$

The substances A, B. , M, N. . are in chemical equilibrium as expressed by the equation

$$aA + bB + \ldots \rightleftarrows mM + nN + \ldots$$

The partial pressures of the substances taking part in the equilibrium act through suitable semipermeable membranes against the pistons as follows: p_A against piston **A**, p_B against piston **B**, p_M against piston **M** and p_N against piston **N**. The total pressure on the system is applied by means of piston **D**.

Chamber **E′**: Analogous in every respect to chamber **E** except that the equilibrium has been slightly displaced by some cause so that the partial pressures from this chamber have become $p_A + dp_A$ against piston **A′**, $p_B + dp_B$ against piston **B′**, etc.

[For a liquid (or solid) phase in the chamber, the cylinders are filled with the pure substances A, B, M, N, etc., in the liquid (or solid) state and the pressures on the pistons are osmotic pressures, Π_A and $\Pi_A + d\Pi_A$, Π_B and $\Pi_B + d\Pi_B$, etc.]

The operation of the engine consists in the movement of pistons **AA′**

and **BB′** toward the left until a mols of A and b mols of B have been forced into **E** and drawn out of **E′**; and the simultaneous movement of pistons **MM′** and **NN′** toward the right, removing m mols of M and n mols of N from **E** (as fast as they are formed by the reaction of A and B which are being introduced by pistons **AA′** and **BB′**) and forcing them into **E′** (as fast as they are required to replace, by reaction, the A and B which are being removed by pistons **AA′** and **BB′**). The equilibrium is not disturbed in either chamber. The work done by pistons **AA′**, **BB′**, **MM′** and **NN′** is

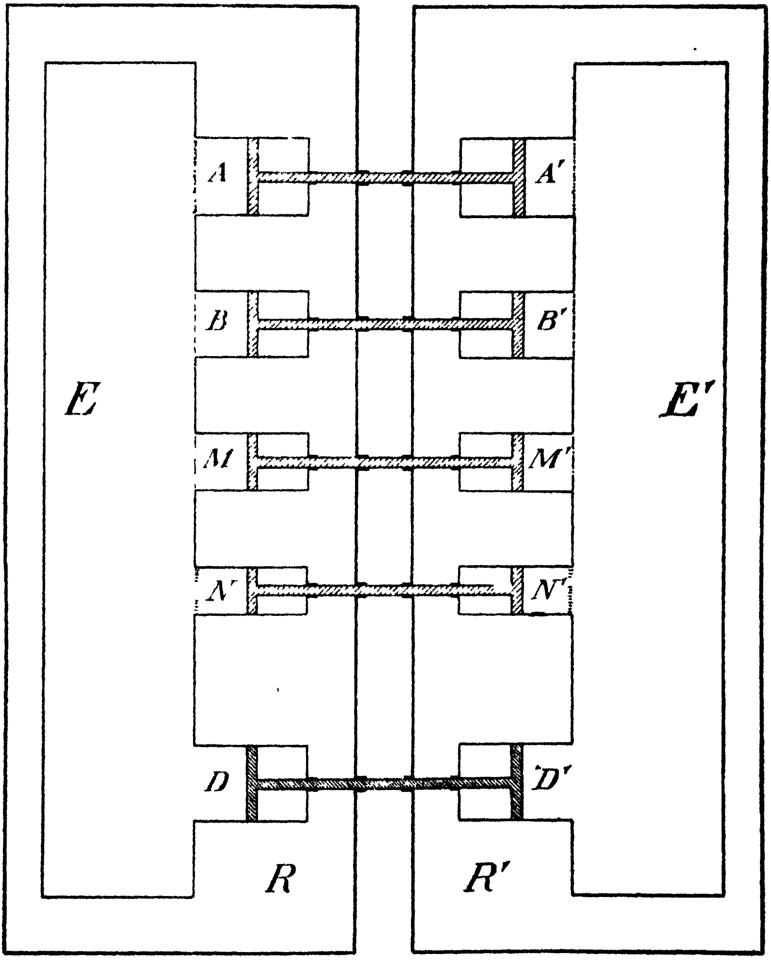


Fig. 2.

$$av_A dp_A + bv_B dp_B + \ldots - mv_M dp_M - nv_N dp_N - \ldots,$$

or more briefly,

$$\Sigma\pm av_{\mathrm{A}}dp_{\mathrm{A}} \quad [\text{for liquid or solid, } \Sigma\mp aV_{\mathrm{A}}d\Pi_{\mathrm{A}}].$$

The ± sign indicates that terms relating to the reacting substances are to be taken with a positive sign and those relating to the products of the reaction with a negative sign.

By the Second Law (Theorems I and II), this work is equal to (1) zero, or (2) QdT/T according as the displacement of the equilibrium in chamber **E′** is brought about by changing (1) the composition, or the total pressure, or (2) the temperature. We shall consider each effect separately.

The Composition and Pressure Coefficients (P, T = *const. or* N, T = *const*).—Keep the *total pressure* and the temperature in **E** and **E′** the same and displace the equilibrium in **E′** by changing the mol fraction of (say) A from N_{A} to $N_{\mathrm{A}} + dN_{\mathrm{A}}$; *or*, keep the *composition* and temperature the same in both **E** and **E′** and change the total pressure on **E′** from P to $P + dP$ by means of piston **D′**. In either case the operation of the engine gives us at once the equation

$$av_{\mathrm{A}}dp_{\mathrm{A}} + bv_{\mathrm{B}}dp_{\mathrm{B}} + \ldots - mv_{\mathrm{M}}dp_{\mathrm{M}} - nv_{\mathrm{N}}dp_{\mathrm{N}} - \ldots = 0 \quad (29)$$

or

$$\left(\frac{\Sigma\pm av_{\mathrm{A}}\partial p_{\mathrm{A}}}{\partial N_{\mathrm{A}}}\right)_{P,T} = 0 \quad (30) \qquad \left[\left(\frac{\Sigma\mp aV_{\mathrm{A}}\partial\Pi_{\mathrm{A}}}{\partial N_{\mathrm{A}}}\right)_{P,T} = 0 \quad (30a)\right.$$

$$\left(\frac{\Sigma\pm av_{\mathrm{A}}\partial p_{\mathrm{A}}}{\partial P}\right)_{N,T} = 0 \quad (31) \qquad \left.\left(\frac{\Sigma\mp aV_{\mathrm{A}}\partial\Pi_{\mathrm{A}}}{\partial P}\right)_{N,T} = 0 \quad (31a)\right]$$

These equations contain everything which thermodynamics alone is capable of teaching us concerning a chemical equilibrium at constant temperature. To proceed further it is necessary to know the functional relation between p and v for the system under consideration. To illustrate, let us assume that this relation is $pv = RT$, *i. e.*, the perfect gas law. Putting $v_{\mathrm{X}} = RT/p_{\mathrm{X}}$ for each substance in equation (30), the equation becomes

$$RT\,d\ln\frac{p_{\mathrm{A}}^{a}\cdot p_{\mathrm{B}}^{b}\cdots}{p_{\mathrm{M}}^{m}\cdot p_{\mathrm{N}}^{n}\cdots} = 0. \quad (32)$$

This equation can obviously only be true if

$$\frac{p_{\mathrm{A}}^{a}\cdot p_{\mathrm{B}}^{b}\cdots}{p_{\mathrm{M}}^{m}\cdot p_{\mathrm{N}}^{n}\cdots} = const. = K_{p}, \quad (33)$$

which is the mathematical formulation of the law of chemical mass action in terms of partial pressures. It can be expressed in terms of *mol fractions* or *volume concentrations* by substituting $p_{\mathrm{X}} = N_{\mathrm{X}}P$ or $p_{\mathrm{X}} = C_{\mathrm{X}}RT$, respectively, in equation (33), giving

$$\frac{N_{\mathrm{A}}^{a}\cdot N_{\mathrm{B}}^{b}\cdots}{N_{\mathrm{M}}^{m}\cdot N_{\mathrm{N}}^{n}\cdots} = K_{p}P^{\Delta x}(= K_{N} \text{ for constant } P), \quad (34)$$

and

$$\frac{C_A^a \cdot C_B^b \cdots}{C_M^m \cdot C_N^n \cdots} = K_p(RT)^{\Delta x} = K_C, \qquad (35)$$

where Δx—the change in the number of mols which results from the reaction—is written for $(m + n + \ldots - a - b - \ldots)$.

It is evident, from the preceding, that the Law of Mass Action for a gaseous phase (*i. e.*, equation (33)) expresses the condition of chemical equilibrium *only* for a system in which the substances taking part in the reaction are all perfect gases. And of the perfect gas laws only those of Boyle and Avogadro are involved. It is not essential that the law of Gay-Lussac (*i. e.*, $p = kT$) be obeyed. To state, therefore, that any chemical equilibrium (in a gaseous phase or dilute solution) does not obey the Mass Action Law is simply to state that the pressure (gaseous or osmotic) of at least *one* of the substances concerned in the equilibrium does not obey the law of Boyle-Avogadro. Notwithstanding the fact that this law has been shown to be both a necessary and sufficient condition for the validity of the Law of Mass Action, the belief seems still to be held in some quarters that the latter law may after all have a wider and more general application. T. B. Robertson, for example, in a recent paper,[8] considers the conditions for chemical equilibrium in a system in which the equation $p(v - d) = RT$ is obeyed instead of the perfect gas law. He concludes that such a system must *also* obey the Law of Mass Action.[9] This conclusion must be regarded as erroneous. The equation $p(v - d) = RT$ does *not* lead to the Mass Action Law but to quite a different expression, as will be evident by substituting $v = RT/p + d$, in equation (30) and integrating. This gives the relation

$$RT \ln p_A^a \cdot p_B^b \cdots / p_M^m \cdot p_N^n \cdots = const. - \Sigma \pm a p_A d_A \qquad (36)$$

in which the last term represents the series

$$a p_A d_A + b p_B d_B + \ldots - m p_M d_M - n p_N d_N - \ldots$$

Similarly for *each* equation of state there is a *corresponding* law of chemical equilibrium but the Law of Mass Action belongs *only* to systems obeying the Boyle-Avogadro law.

The Temperature Coefficient $(P,\ N = const.)$.—Keep the composition and total pressure the same in **E** and **E**′ and displace the equilibrium in **E**′ by changing the temperature of **R**′ from T to $T + dT$. The operation of the engine gives us the equation

$$a v_A dp_A + b v_B dp_B + \ldots - m v_M dp_M - n v_N dp_N - \ldots = Q dT/T \qquad (37)$$

or

---

[8] *J. Physic. Chem.*, 10, 522 (1907).

[9] This conclusion seems to have been accepted by other investigators, apparently without question. It is quoted by the Earl of Berkeley (*Proc. Roy. Soc.*, A79, 131 (1907)) in support of certain conclusions regarding the application of van der Waals' equation to solutions and it is even beginning to appear in the text-books. See, for example, the last edition of Morgan's "Elements of Physical Chemistry," p. 239.

$$\left(\frac{\Sigma^{\pm} a v_A \partial p_A}{\partial T}\right)_{P,[N-f(T)]} = \frac{Q_p}{T} \quad (38) \quad \left[\left(\frac{\Sigma^{\pm} a V_A \partial \Pi_A}{\partial T}\right)_{P,[N-f(T)]} = \frac{Q_\pi}{T} \quad (38a)\right]$$

where Q_p is the heat *evolved* by the reaction when it proceeds from left to right according to equation (27) and does the maximum external work. If we assume the *perfect gas law* this equation becomes

$$(\partial \ln K_p/\partial T)_{P,N} = Q_p/RT^2, \tag{39}$$

where K_p is defined by equation (33). We may substitute, $K_p = K_c(RT)^{\Delta x}$ (equation (35)) and $Q_p = U - \Delta xRT$ (by the first law of thermodynamics) and obtain the familiar equation of van't Hoff,

$$d\ln K_c/dT = U/RT^2, \tag{40}$$

where K_c is defined by equation (35) and U, the change in total energy, is the heat evolved when the reaction takes place (from left to right) without external work.[10]

6. Chemical Equilibrium. B. Heterogeneous.

The Composition Coefficient (*P*, *T* = *const.*).—The arrangement and operation of the engine for this case are in general exactly the same as for the corresponding case of homogeneous equilibrium, except that

---

[10] General Equations.—The results just obtained for the effects of composition, pressure and temperature can, if desired, be expressed in a single general equation. For example, suppose we wish to find a general equation by means of which K_N can be calculated for a given gaseous mixture at any temperature or pressure. We have the general expression

$$d\ln K_N = (\partial \ln K_N/\partial P)_T dP + (\partial \ln K_N/\partial T)_P dT. \tag{41}$$

From equation (34), by taking the logarithm of both sides and differentiating, we obtain

$$(\partial \ln K_N/\partial P)_T = \Delta x/P. \tag{42}$$

From equations (34) and (39) we obtain

$$(\partial \ln K_N/\partial T)_P = (\partial \ln K_p/\partial T)_P = Q_p/RT^2. \tag{43}$$

But by the first law of thermodynamics,

$$Q_p/RT^2 = U + \Delta xRT/RT^2 = U/RT^2 + \Delta x/T \tag{44}$$

and

$$U = U_0 + \Sigma(ah_A)T. \tag{45}$$

Consequently,

$$(\partial \ln K_N/\partial T)_P = U_0/RT^2 + \Sigma(ah_A)/RT + \Delta x/T \tag{46}$$

and combining with (41) and (42) we obtain finally,

$$d\ln K_N = \Delta x dP/P + U_0 dT/RT^2 + [\Sigma(ah_A) + R\Delta x]dT/RT \tag{47}$$

which, on integration, yields

$$\ln K_N = \ln I + \Delta x \ln P + \frac{(\Sigma(ah_A) + R\Delta x)}{R}\ln T - \frac{U_0}{RT} \tag{48}$$

or, written in the exponential form

$$K_N = IT^b P^{\Delta x} e^{-\frac{U_0}{RT}} \tag{49}$$

in which I is the integration constant and b is written for $(\Sigma(ah_A) + R\Delta x)/R$. This is Gibbs' formula for gas dissociation, and has, I believe, heretofore never been derived except by the use of Gibbs' thermodynamic potential. Van Laar even goes so far as to state (*Sechs Vorträge*, p. 69) that it is not possible to derive it in any other way.

substances present in a second state of aggregation are not removed from one chamber and forced into the other during the operation of the engine, but are simply allowed to vaporize (or dissolve) in one chamber and condense (or precipitate) in the other as the reaction progresses. This, of course, necessitates the movement of the pressure piston, **DD′**, through the corresponding volume change; but since it moves under zero pressure it does no work, and the differential equation obtained is therefore identical with the one for homogeneous equilibrium *with the omission of all terms referring to substances present in a second state of aggregation.* These omissions may be indicated by placing the symbol $\textcircled{2}$ inside the summation sign. Thus in place of equation (30) [and (30*a*)] we have:

$$\left(\frac{\Sigma_{\textcircled{2}} a v_A \partial p_A}{\partial N_A}\right)_{P,T} = 0 \quad (50) \qquad \left[\left(\frac{\Sigma_{\textcircled{2}} a V_A \partial \Pi_A}{\partial N_A}\right)_{P,T} = 0\right] \quad (50a)$$

It is customary to derive the laws of heterogeneous chemical equilibrium, from the corresponding laws of homogeneous equilibrium—the Mass Action Law for example—by assuming that the pressures or concentrations of substances present in a second state of aggregation are constants. While this gives the correct result and is a convenient aid to the memory, as a general method of proof it must be condemned, because the assumption upon which it is based is not only unnecessary but is apt to be misleading. This can be illustrated by considering a specific example.

The law of the constancy of the solubility product for difficultly soluble substances which dissociate in solution is almost invariably derived by first assuming the Mass Action Law and then assuming that the concentration of the undissociated portion is a constant so long as an excess of the solid phase is present. Now in the case of aqueous solutions of strong electrolytes, Stieglitz has recently called attention to the fact that since the Mass Action Law does not hold even approximately for these substances, any derivation based upon this law cannot be applied to their solutions. He therefore concludes[11] that there is no theoretical basis for the Solubility Product Law in the case of strong electrolytes.

This criticism of the method of derivation in the case of strong electrolytes is quite justified, but the conclusion which is drawn regarding the lack of theoretical foundation for the law in these cases is unjustified. In order to derive the Solubility Product Law it is not only unnecesssary to assume the Mass Action Law but it is not even necessary to know what the law is which regulates the equilibrium between the dissociated and undissociated portions of the dissolved solute. This can be made clear by applying the engine as indicated above (p. 487) to a saturated solution of a solute, BC for example, which dissociates in solution according to the equation

---

[11] Stieglitz, THIS JOURNAL, 30, 954 (1908). After recalculating Arrhenius' solubility data and finding good agreement with the Solubility Product Law, he concludes: "In view of these facts and also in view of the results of the complete calculation of Arrhenius' data on the solubility of the silver salts, which removed the last *theoretical* foundation for the solubility product constant, we may well consider it for the present to be an approximate empirical principle."

$$BC \rightleftarrows B + C.$$

We obtain at once the equation[12]

$$V_B d\Pi_B + V_C d\Pi_C = 0 \qquad (51)$$

where $d\Pi$ in both cases may be *either* $(\partial\Pi/\partial N_B)dN_B$ or $(\partial\Pi/\partial N_C)dN_C$.

If A and B are "normal solutes" and the solution is sufficiently dilute it can be readily shown that equation (51) takes the form

$$C_{B'} \cdot C_{C'} = const. = (\alpha_0 S_0)^2 \qquad (53)$$

---

[12] If the operation is carried out in the manner described in the preceding sections, the cylinders of the engine will contain pure liquid B (resp. C) and π_B (resp. π_C) will denote the difference in pressure upon the solution and the pure liquid B (resp. C) which is necessary to establish equilibrium; or as we have called it (see p. 478), "the osmotic pressure referred to B (resp. C) as the solvent." In case B and C happen to be ions, some difficulty will doubtless arise in the minds of some readers as to the validity of a process which makes use of a cylinder filled with pure liquid ion. If so, the arrangement of the engine can be easily changed so that the cylinders shall contain *solutions* of the ions separated from the chambers by membranes permeable only to the ion in question. The pistons then would be permeable only to the solvent and the osmotic pressure (π_B' resp. π_C') would be the *ordinary* osmotic pressure of the solute, in the present instance an ion. Thus, looking at Fig. 3 a moment, the movement of piston BB′ toward the left would necessitate the flow of pure solvent toward the right through piston B′ into cylinder B′ where it would dilute the solution of B-ion contained in this cylinder. But this solution would then no longer be in equilibrium with the solution in chamber E′ and the ion B^+ would pass from E′ through the semipermeable membrane into cylinder B′ until the equilibrium was restored. The motion of piston BB′ toward the left would therefore result in drawing B^+-ion out of chamber E′ and forcing it into Chamber E, just as in the general case where the cylinders are filled with the pure liquids. Piston CC′ would do the same for C-ion, so that we would obtain the equation

$$V_{B'} d\pi'_{B'} + V_{C'} d\pi'_{C'} = 0, \qquad (52)$$

which is identical in form with equation (51) above and for dilute solutions leads to the same result when integrated. Thus if the ions are "normal solutes" and the solution is "sufficiently dilute," we can write for each ion

$$\pi' = CRT,\ d\pi' = RTdC \text{ and } V = 1/C$$

which gives us

$$RTd \ln C_{B'} \cdot C_{C'} = 0,$$

or

$$C_{B'} . C_{C'} = \text{const} = (\alpha_0 S_0)^2. \qquad (53)$$

The exact significance of the term "normal solute" will be treated more fully in a future communication, in which a set of equations for solutions will be derived without making any assumption regarding the concentration of the solution. The equations for "dilute solutions" which are developed in the present paper will there be shown to be only special cases of a more general set of equations for solutions of any concentration. For the present the term "normal solute" may be understood to refer to any solute "whose osmotic pressure in dilute solution obeys the gas laws."

which is the Solubility Product Law. S_0 and α_0 are, respectively, the solubility of BC in the pure solvent and its degree of dissociation in this solution. Since the Solubility Product Law is found to hold, at least approximately, for solutions of strong electrolytes of the uni-univalent type, it is evidence that the ions in these solutions are approximately "normal solutes" (*i. e.*, their osmotic pressures are proportional to their concentrations in dilute solution), and that the deviations from the Mass Action Law for strong electrolytes must be attributed *chiefly* to the failure of the Boyle-Avogadro law in the case of the unionized molecules. This conclusion has been pointed out recently by A. A. Noyes,[13] who offers a very suggestive provisional hypothesis to account for the abnormal behavior of the unionized molecules in such solutions.

The Pressure Coefficient (N, T = *const.*).—In the case of heterogeneous equilibrium, when piston **DD′** applies a pressure P to chamber **E** and $P + dP$ to chamber **E′**, the operation of the engine is accompanied by a motion of this piston through the volume change which results from the chemical reaction and a work term, ΔVdP, appears in the equation which was absent in the corresponding case of homogeneous equilibrium (q. v. p. 484). Otherwise the operation remains the same and the final equation obtained is in all other respects identical with the corresponding one for homogeneous equilibrium, but *with the omission of all terms referring to substances present in a second state of aggregation.* Thus, corresponding to equation (31) [and (31*a*)] for homogeneous equilibrium, we obtain in the case of heterogeneous equilibrium the equation

$$\left(\frac{\Sigma_{(2)}^{\pm} av_A\partial p_A}{\partial P}\right)_{N,T} = \Delta V \quad (54) \text{ and } \left[\left(\frac{\Sigma_{(2)}^{\pm} aV_A\partial \Pi_A}{\partial P}\right)_{N,T} = \Delta V_\pi\right]. \quad (54a)$$

The exact meaning of ΔV is clearly evident from the operation of the engine. It is equal to the increase in the total reaction volume of all substances present in a second state of aggregation, which results when the reaction proceeds from left to right in the sense of equation (27). This can be illustrated by considering some specific examples.

Suppose the reaction under consideration is

$$a\text{A} + b\text{B} \rightleftarrows m\text{M} + n\text{N} \qquad (55)$$

in which A and M are gases and B and N solids. Applying equation (54) to this case, or better, using the engine directly, we obtain the equation

$$av_A dp_A - mv_M dp_M = \Delta V dP. \qquad (56)$$

ΔV here is obviously equal to the reaction volume of N minus the reaction volume of B. Now the reaction volume of N is nV_N, where V_N is the molecular volume of *solid N* under the pressure P. Similarly the reaction volume of B is bV_B, so that $\Delta V = nV_N - bV_B$. If we assume the perfect gas laws for A and M, equation (56) becomes

---

[13] A. A. Noyes, THIS JOURNAL, 30, 351 (1908).

$$RTd\ln p_A^a/p_M^m = (nV_N - bV_B)dP \tag{57}$$

or

$$(\partial \ln K_p/\partial P)_{T,N} = (nV_N - bV_B)/RT. \tag{58}$$

Another example: Let us consider a solid BC in contact with its saturated solution in which it exists in a state of partial dissociation, the equilibrium between the solid and its dissociation products in solution being expressed by the equation

$$\mathrm{BC} \rightleftarrows \mathrm{B} + \mathrm{C}. \tag{59}$$

How will an increase of pressure affect this equilibrium? Operate the engine so that solid BC dissolves in chamber **E′**, under the pressure $P + dP$ and its dissociation products are removed osmotically and an equivalent amount forced into chamber **E**, where they at once combine to form solid BC under the pressure P. This gives us the equation

$$V_B d\Pi_B + V_C d\Pi_C = \Delta V dP, \tag{60}$$

in which ΔV is the decrease in volume which results when one reaction weight (= one mol in this case) of solid BC dissolves in its saturated solution. If B and C are "normal solutes"[12] and the solution is dilute it can be shown that equation (60) becomes

$$RTd\ln(\alpha_0 S_0)^2 = \Delta V dP \tag{61}$$

or

$$[\partial \ln(\alpha_0 S_0)^2/\partial P]_{N,T} = \Delta V/RT \tag{62}$$

in which S_0 is the solubility of BC (expressed as mols per 1000 grams of solvent) under the pressure P and α_0 is its degree of dissociation in the saturated solution. This is obviously an equation giving the pressure coefficient of the logarithm of the solubility product.[19]

The Temperature Coefficient (N, P, = *const.*).—From what has been said in the preceding portions of this section, it is evident that the operation of the engine for this case gives us the general equation

$$\left(\frac{\Sigma \overset{+}{\underset{\smile}{(2)}} av_A \partial p_A}{\partial T}\right)_{N,P} = \frac{QdT}{T} \quad (63), \quad \left[\left(\frac{\Sigma \overset{+}{\underset{\smile}{(2)}} aV_A \partial \Pi_A}{\partial T}\right)_{N,P} = \frac{Q_\pi dT}{T}\right]. \quad (63a)$$

We will reserve until some future time the further discussion of the general case, and will consider here a specific example, the temperature coefficient of the solubility product for an electrolyte.

---

[19] In case B and C happen to be ions we may modify the operation of the engine as explained in note (12). In this case we shall, however, obtain the same final equations (*i. e.*, equation (62)).

Let us apply the engine directly: We have in both chambers a saturated solution of an electrolyte BC in contact with an excess of the solid. Chamber **E** is at $T°$ and chamber **E′** at $T + dT°$. The operation of the engine consists in the solution of one mol of solid BC in chamber **E′**, accompanied by its simultaneous removal osmotically in the form of solutious of B-ion and C-ion by means of pistons **B′** and **C′**, as described in note 12. The reverse process, of course, occurs in chamber **E**. The equation for the operation is (cf. eq. 52).

$$V_{B'}d\Pi'_{B'} + V_{C'}d\Pi'_{C'} = QdT/T \tag{64}$$

If the ions as "normal solutes" and the solution is "sufficiently dilute" we can write for each ion, $\Pi' = CRT$, $d\Pi' = RTdC + RCdT$, and $V = 1/C$,
which gives

$$RTd\ln C_{B'}.C_{C'} + 2RdT = QdT/T, \tag{65}$$

or

$$RT^2d\ln(\alpha_0.S_0)^2 = (Q - 2RT)dT, \tag{66}$$

or

$$(\partial\ln(\alpha_0.S_0)^2/\partial T)_{P,N} = U/RT^2. \tag{67}$$

U, the increase in internal energy, is equal to the heat absorbed when a system composed of one mol of solid BC and $1000/2\alpha_0.S_0$ grams of pure solvent, both under the pressure P and at the temperature T, changes, without the production of any work, into a system composed of a solution of BC in which the solute exists only in the form of its ions. Such a solution cannot be obtained in reality but the corresponding heat effect can be measured, which is all that is necessary. It is perhaps worth while to consider a numerical example illustrating the use of equation (67).

Let us compare the directly measured value of U with the value calculated by means of the expression

$$2RT^2(d\ln\alpha_0/dT + d\ln S_0/dT) = U, \tag{68}$$

in the case of orthonitrobenzoic acid. The value of U for this acid obtained by calorimetric measurements at 20° is 4040 ± 100 cal.[14] The value of $(d\ln S_0/dT)_{20°}$ has been determined by Noyes and Sammet[15] and found to be 0.03335. From their conductivity measurements at 15° and 25°, we obtain $\alpha_{15°} = 0.386$ and $\alpha_{25°} = 0.311$, whence $\Delta\ln\alpha/\Delta t$ for this temperature interval comes out —0.0216, which we shall take as the value of $(d\ln\alpha_0/dT)_{20°}$. Adding these values we obtain $d\ln(\alpha_0 S_0)/dT = 0.0118$, which, when multiplied by $2RT^2$ (*i. e.*, $2 \times 1.98 \times 293 \times 293$) gives 4020 Cal. as the calculated value of U, which is in good agreement with the directly measured value.

---

[14] From a determination made in this laboratory by Mr. D. A. MacInnes. We hope to extend this investigation in the near future and will therefore defer the description of the method until its completion.

[15] Noyes and Sammet, *Z. physik. Chem.*, 43, 529 (1903).

In interpreting their experimental results, Noyes and Sammet use the equation of van't Hoff[16] for the temperature coefficient of the *total* concentration of a saturated solution of an ionized solute, namely,

$$d\ln iS/dT = L/iRT^2, \qquad (69)$$

in which i ($= 1 + \alpha$) is the van't Hoff coefficient. We would have obtained this equation, if in using the engine we had removed osmotically from chamber E′ not simply one mol of the solute in the form of its ions but one mol of the solute in the form of both ions and undissociated molecules, in the proportions in which they exist together in the saturated solution. Then, in order to obtain the equation in the above form, we should have had to assume that the undissociated molecules were "normal solutes" as well as the ions. In other words, the van't Hoff equation involves an unnecessary number of assumptions. It is an equation which can be obtained by combining two equations, one involving only the ions (*i. e.*, equation (67)) and another similar one involving only the undissociated molecules.

The recent work of A. A. Noyes and his associates[17] has shown us the necessity for differentiating between ions and undissociated molecules with regard to their behavior as solutes. There is all the more reason for doing this since the assumption that they behave alike in this respect is quite unnecessary in the majority of cases. All of our equations for solution, which contain the van't Hoff factor i, are derived on the assumption that both ions and undissociated molecules are "normal solutes." Consequently, if a given equation is found to be in agreement with the results of experiment, it does not necessarily mean that this assumption is correct, for agreement might still occur if both the ions and undissociated molecules deviated, but in opposite directions, from the behavior of the normal solute. If the equation is not in agreement with the results of experiment, it does not tell us whether the disagreement is due to the behavior of the ions or the undissociated molecules, or both. And yet it is quite possible to decide this question, for in nearly every case the equation containing the van't Hoff i can be broken up into two simpler equations, one of which involves only the ions and the other only the undissociated molecules. An example of this occurs in the case of orthonitrobenzoic acid, described above. Noyes and Sammet found that the van't Hoff equation (eq. (69)) *was not* in agreement with the results of their experiments with this acid. We have seen that equation (67), which involves only the ions, *is* in good agreement with the experimental results. Consequently the deviation from the van't Hoff equation must be ascribed, for the most part at any rate, to the abnormal behavior of the undissociated portion. Whether it is to be attributed to the partial association of the unionized molecules (as Noyes and Sammet suggest) or to the presence of two isomeric forms of these molecules is not yet certain.[18]

---

[16] van't Hoff, *Z. physik. Chem.*, 17, 147, 546 (1895).

[17] Carnegie Inst. Pub., No. 63.

Before leaving this subject attention should be called to the fact that we have in equation (67) a very valuable method for studying the behavior of ions (apart from the unionized molecules) with respect to the Gay-Lussac law for the effect of temperature upon osmotic pressure in dilute solutions.[18]

7. Electromotive Force.

The Perfect Thermodynamic Engine is generally applicable to the derivation of all types of electromotive force equations which are based directly upon the Second Law In the present paper, however, we shall confine the consideration to the electromotive force of concentration cells. The type of engine used is shown in Fig. 3. It differs from the preceding forms only by the addition of the parts **W** and $\eta\eta'$. **W** is a device which permits the easy passage of ions but which resists any mass flow of the solution from one chamber to the other, thus permitting a difference of pressure to be maintained in the two chambers, if desired. η and η' are two reversible electrodes which can be connected with each other (through a suitable compensating external E. M. F. to ensure operation under equilibrium) by means of the key **K**.

Concentration Cells (T, P = *const*.).—(*a*) *The Nernst Equation.*—As an example of this case let us consider a simple concentration cell with reversible silver electrodes and with silver nitrate as the electrolyte. Using the engine shown in Fig. 3, omitting cylinder **AA'**, and with temperature of **R** and **R'** = T, and pressure against **D** and **D'** = P, the arrangement of the engine is as follows:

Chamber **E**: Filled with a solution of silver nitrate of concentration C and provided with a reversible silver electrode η which has a potential E. Cylinder **B** contains a solution of silver ion which is in equilibrium, through the semipermeable membrane, with the silver ion in the chamber. Piston **B**, which is impermeable only to silver ion, is under the "osmotic pressure" $\Pi'_{Ag^{\cdot}}$. Cylinder **C** is arranged similarly with respect to NO_3-ion, the "osmotic pressure" against piston **C** being $\Pi'_{NO'_3}$.

Chámber **E'**: Similar to **E** except that the solution has concentration $C + dC$, the potential of the electrode η' is E + dE and the osmotic pressures are $\Pi'_{Ag^\cdot} + d\Pi'_{Ag^\cdot}$ against piston **B′** and $\Pi'_{NO'_3} + d\Pi'_{NO'_3}$ against piston **C′**.

---

[18] We hope to pursue this question further experimentally in this laboratory, as well as the general question of the temperature coefficients of the osmotic pressures of ions as distinct from the unionized molecules.

To operate the engine, close the key **K** and allow one equivalent (F) of electricity to flow reversibly. The passage of this current is accompanied by the electrical transference of n_a equivalents of electrolyte from chamber **E′** to chamber **E** (*i. e.*, from cathode to anode). n_a is the ordinary or Hittorf transference number of the anion.[20] To compensate

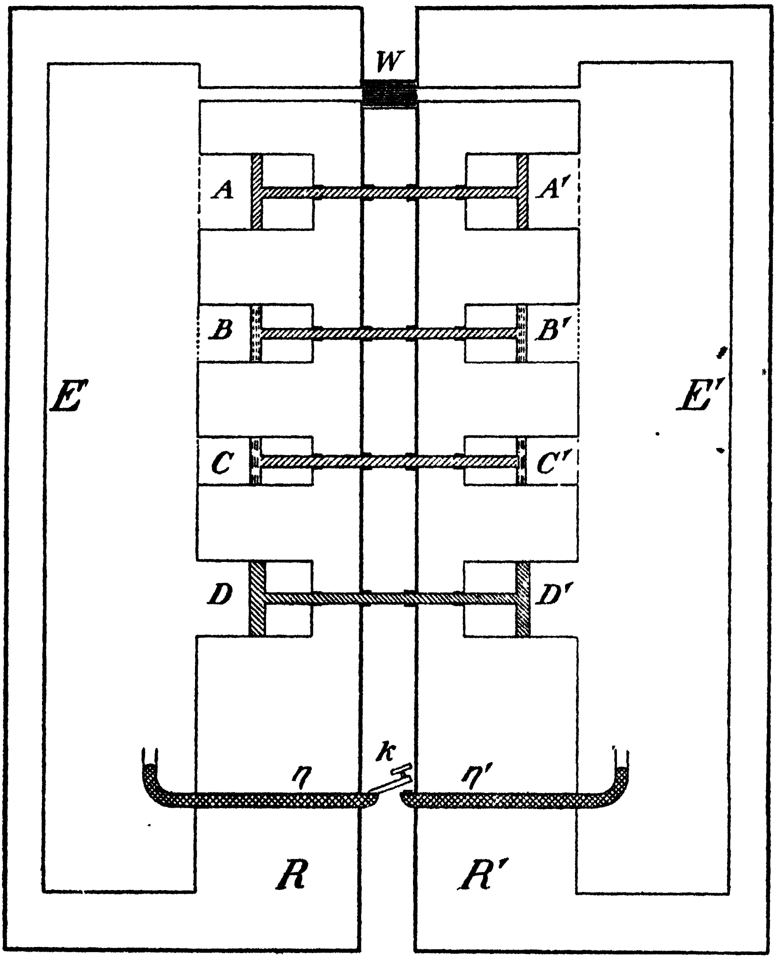


Fig. 3.

---

[20] In general, both solvent and electrolyte are transferred by the current. For the present purpose it is not necessary to differentiate between these two factors but only to know the *total* effect referred to solute alone, and this is expressed by the ordinary Hittorf transference number. An equation involving the "true transference number" (see Washburn, THIS JOURNAL, 31, 323 (1909)) can be readily obtained by

for this effect and maintain equilibrium, pistons **BB′** and **CC′** move reversibly toward the right removing n_a mols of each ion from **E** and forcing them into **E′**. By the Second Law the total work is equal to zero, or

$$FdE = n_a[V_{Ag^{\cdot}}d\Pi'_{Ag^{\cdot}} + V_{NO_3'}d\Pi'_{NO_3'}]. \qquad (70)$$

If we assume the ions to be normal solutes and the solution dilute, this equation becomes

$$dE = (2n_aRT/F)d\ln C_{Ag^{\cdot}}. \qquad (71)$$

In order to integrate we need to know n_a as a function of $C_{Ag^{\cdot}}$. If we assume it to be independent of the concentration we obtain the Nernst equation on integrating.

$$E - E' = \Delta E = (2n_aRT/F)\ln C_{Ag^{\cdot}}/C'_{Ag^{\cdot}}. \qquad (72)$$

If $C_{Ag^{\cdot}} = \alpha C$ and $\alpha = \Lambda_c/\Lambda_\infty$ this equation becomes

$$E - E' = \Delta E = (2n_aRT/F)\ln \Lambda_cC/\Lambda_{c'}C', \qquad (73)$$

in which Λ_c indicates the equivalent conductance of the solution at the concentration C.

It should be noticed that *this equation contains no assumption regarding the relation which exists between the ions and undissociated molecules in the solution.* It requires only that the ions be "normal solutes," the behavior of the undissociated molecules in this respect not being involved. Another important characteristic of the equation is the fact that *it is not influenced by errors in the value of the equivalent conductance at infinite dilution.* It offers therefore *another* method of studying the behavior of ions apart from their relation to the undissociated molecules (cf. page 489).

(*b*) *The Helmholtz Equation.*—Using the engine shown in Fig. 3 but omitting cylinders **BB′** and **CC′** the arrangement is as follows:

Chamber **E**: Filled with a solution of (say) HCl of any concentration C and provided with a reversible calomel electrode η having the potential E. The vapor pressure of HCl from the solution acts through the semipermeable membrane against piston **A** with a pressure p.

Chamber **E′**: The same as **E** except that the concentration of the solution is $C + dC$, the potential of η' is $E + dE$ and the vapor pressure acting against piston **A′** is $p + dp$.

The operation of the engine is evident and gives us at once the relation

$$FdE = n_Kvdp. \qquad (74)$$

If the vapor obeys the perfect gas law this becomes

$$dE = (n_KRT/F)d\ln p \qquad (75)$$

which on integration, assuming n_K const., gives the Helmholtz equation,

$$E - E' = (n_KRT/F)\ln p/p'. \qquad (76)$$

---

introducing into the engine a vapor piston by means of which solvent can be vaporized from one chamber and condensed into the other.

n_K is here the Hittorf transference number of the cation. Obviously an exactly similar equation can be obtained in terms of the partial vapor pressures of the *solvent* from the two solutions.

These two examples will be sufficient to illustrate the use of the engine in deriving E. M. F. equations. The requisite arrangement and operation of the engine for the derivation of pressure or temperature equations (*e. g.*, the Gibbs-Helmholtz equation) will be readily understood from the corresponding cases of vapor pressure, chemical equilibrium, etc., which have been described in the preceding pages.

8. The Colligative Properties of a Solution.

The quantities osmotic pressure, vapor-pressure lowering, freezing-point lowering, boiling-point raising,[21] etc., which lie at the basis of our methods of molecular weight determination in solution, have played such important rôles in the development of the modern theory of solutions, that a clear conception of the thermodynamic relations which connect them with one another is of fundamental importance. In many cases, the derivations of these relations which are given in the text-books contain the assumption that the solution is dilute and involve one of the laws of dilute solutions. Even in an elementary text, the only excuse that can be offered for introducing such assumptions is that the derivation of the exact relation is too complicated for the student to grasp at this stage. But even on such grounds, this procedure can scarcely be justified if it leaves the student with the idea that the relation between osmotic pressure and freezing-point lowering, for example, is in any way dependent upon the law which connects either of these quantities with the concentration. In the following pages it will be shown that by means of the thermodynamic engine the exact relations can be written down at once. These relations are, of course, differential equations. The method of integration varies with the nature of the solvent and the accuracy with which it is possible to measure the various quantities concerned. In the present paper the methods of integration will only be indicated briefly for some of the simplest cases.

The type of engine used is shown in Fig. 1. Both chambers are filled with the solution under investigation. Piston **AA′** is a "vapor piston," that is, as it moves toward the left, for example, it draws the vapor of the solvent out of chamber **E′** and condenses it into chamber **E**. Piston **BB′** is an osmotic piston. As it moves toward the left it allows solvent to enter chamber **E′** by passing through the semipermeable head **B′**, while at the same time solvent is removed in a similar manner from chamber **E**, the space behind the two piston heads being filled with pure solvent. Piston DD′ is the total pressure piston. It moves to the right or left during the operation of the engine whenever a volume change in the chambers renders it necessary, but since in the following treatment we shall deal always with a solution under constant external pressure (that of the atmosphere for example), this piston will move only under a pressure difference of zero. Consequently no work is involved in its motion and it will not be necessary to consider it at all during the operation of the engine.

---

[21] Following the suggestion of Ostwald, we shall call these quantities the colligative properties of the solution.

For the solution we will take any homogeneous liquid mixture of any number of constituents, A, B, C, etc. Since the terms solvent and solute are perfectly arbitrary for such a solution, let us regard A as the solvent and the other constituents as solutes.

Osmotic Pressure and Vapor Pressure (P, T = *const.*).—To ask the question, How does the vapor pressure of the solvent from any solution vary with the osmotic pressure? is equivalent to asking the question,[22] How does the vapor pressure of the pure liquid solvent vary with the total pressure upon it? and this relation has already been derived. It is equation (2) which may be written as follows (since by definition $d\Pi = -dP$):

$$(\partial p/\partial \Pi)_{P,T} = -V/v. \qquad (77)$$

In order to integrate we need only know v and V as functions of p and Π, respectively. Assuming the gas laws for the vapor we have $v = RT/p$. If V_0 is the molecular volume of the liquid under the pressure P (*i. e.*, when $\Pi = 0$, see p. 478) and α is its coefficient of compressibility between P and $P - \Pi$ ($\alpha = (V_0 - V)/V_0(P - \Pi - P)$), then $V = V_0(1 + \alpha\Pi)$. Substituting in equation (77) and integrating we have

$$RT\int d\ln p = -V_0\int(1 + \alpha\Pi)d\Pi,$$

or

$$RT\ln p = -V_0(\Pi + {}^1/_2\alpha\Pi^2) + RT\ln p_0,$$

in which the quantity p_0 in the integration constant is the vapor pressure of the pure solvent under the pressure P and at the temperature T. This gives us finally

$$\Pi + {}^1/_2\alpha\Pi^2 = -(RT/V_0)\ln p/p_0. \qquad (78)$$

In many cases the term containing α is negligible and by expanding the logarithm term into a series we can obtain a more convenient form for ordinary use:

$$\Pi \doteq \frac{RT}{V_0}\left[\left(\frac{p_0 - p}{p_0}\right) + {}^1/_2\left(\frac{p_0 - p}{p_0}\right)^2 + {}^1/_3\left(\frac{p_0 - p}{p_0}\right)^3 + \ldots\right] \qquad (79)$$

The ordinary equation for dilute solutions is obtained by neglecting all but the first term in the above series.

---

[22] See the definition of osmotic pressure, p. 478.

Osmotic Pressure and Freezing-point Lowering (P = *const.*).—The problem may be stated thus: How does the osmotic pressure of a solution change with the temperature at which the solution is in equilibrium with the pure solid solvent? The arrangement of the engine is as follows:

Chamber **E**: Filled with a solution in equilibrium with an excess of pure solid solvent and therefore at the temperature of its freezing point, T_F. The mol fraction of the solvent in the solution is N_A. The pure liquid solvent (in cylinder **B**) in equilibrium with the solution is under the osmotic pressure Π.

Chamber **E′**: Exactly as chamber **E** except the mol fraction of the solvent is $N_A + dN_A$, the freezing point $T_F + dT_F$ and the osmotic pressure $\Pi + d\Pi$.

$d\Pi$ in this instance is given by the expression

$$d\Pi = (\partial\Pi/\partial T)_N(\partial T_F/\partial N_A)_P dN_A + (\partial\Pi/\partial N_A)_T dN_A. \qquad (80)$$

To operate the engine allow one mol of solid solvent to melt in chamber **E′** and remove the resulting liquid osmotically with piston **BB′**. The reverse operation occurs in chamber **E′**. The work done by piston **BB′** is $-Vd\Pi$. The heat absorbed at the higher temperature (*i. e.*, from reservoir **R′**) is the molecular heat of fusion (L_F) of the solid solvent, under the pressure P, to form liquid solvent under the pressure $p - \Pi$. We have therefore by the Second Law

$$-Vd\Pi = L_F dT_F/T_F, \qquad (81)$$

or

$$(\partial\Pi/\partial T_F) = -L_F/VT_F. \qquad (82)$$

In this equation we can put $T_F = T_0 - \Delta t_F$, and obtain

$$d\Pi = L_F d(\Delta t_F)/V(T_0 - \Delta t_F), \qquad (83)$$

where Δt_F is the freezing-point lowering in centigrade degrees and T_0 is the freezing point of the pure solvent on the absolute scale.

In order to integrate we need only express V and L_F as functions of Δt_F. V may be expressed by the equation

$$V = V_0 + a\Delta t_F + b(\Delta t_F)^2 + \ldots\ldots \qquad (84)$$

where V_0 is the molecular volume when $\Delta t_F = 0$ and $\Pi = 0$, and a, b, etc., are constants whose numerical values can be computed from the coefficients of compressibility and thermal expansion of the liquid solvent and from approximate values of Π for different values of Δt_F up to the limit desired. For L_F the first law of thermodynamics gives us the general relation,

$$L_F = L_{F_0} + \Delta C_{P_0}\Delta t_F + {}^1/_2\alpha\Delta t_F^2 + {}^1/_3\beta\Delta t_F^3 + \ldots \qquad (85)$$

In this equation L_{F_0} is the molecular heat of fusion of the pure solvent at its freezing point T_0, ΔC_{P_0} is the attendant *decrease* in the heat capacity of the system and α, β, etc., are constants expressing the dependence of ΔC_p upon the temperature.[23]

Substituting equations (84) and (85) in equation (83) and integrating so as to obtain Π as a series function in Δt_F, we obtain the relation

$$\Pi = \frac{L_{F_0}}{V_0T_0}\left[\Delta t_F + {}^1/_2\left(\frac{V_0 - aT_0}{V_0T_0} - \frac{\Delta C_{p_0}}{L_{F_0}}\right)\Delta t_F^2 + {}^1/_3\left(\frac{(V_0 - aT_0)^2}{V_0^2T_0^2} - \frac{\Delta C_{p_0}(V_0 - aT_0)}{L_{F_0}V_0T_0} + \frac{a - bT_0}{V_0T_0} + \frac{{}^1/_2\alpha}{L_{F_0}}\right)\Delta t_F^3 + {}^1/_4\left(\frac{(V_0 - aT_0)^3}{V_0^3T_0^3} - \frac{\Delta C_{p_0}(V_0 - aT_0)^2}{L_{F_0}V_0^2T_0^2} + \frac{(a - bT)(V_0 - aT)}{V_0^2T_0^2} + \frac{{}^1/_2\alpha}{L_{F_0}V_0T_0} + \frac{(V_0 - aT_0)(a - bT_0)}{V_0^2T_0^2} - \frac{\Delta C_{p_0}(a - bT_0)}{L_{F_0}V_0T_0} + \frac{b}{V_0T_0} - \frac{{}^1/_2\beta}{L_{F_0}}\right)\Delta{}_F^4\right]. \quad (86)$$

This apparently cumbersome equation becomes quite simple when we consider a concrete case, owing to the fact that many of the terms in the parentheses are negligible. Let us consider a water solution, for example, and suppose Δt_F to be known with an accuracy of 0.1 per cent. For this case equation (86) becomes

$$\Pi = 12.06(\Delta t_F - 1.78.10^{-3}\Delta t_F^2 - 2.5\ 10^{-6}\Delta t_F^3)\ \text{atmospheres.} \quad (87)$$

This equation can be used for values of Δt_F as high as 100° without introducing an error of more than a few tenths of one per cent.[24]

Osmotic Pressure and Boiling-point Raising (P = *const.*).—The problem may be stated as follows: How does the osmotic pressure change with the temperature at which the partial vapor pressure of the solvent from the solution is equal to the external pressure upon the solution?

The arrangement of the engine is as follows:

---

[23] In the case of water, for example, we have for its molecular heat capacity at constant pressure, $Cp = Cp_0 + at + bt^2 + \ldots$ and for ice $C'_p = C'_{p_0} + a't + b't^2 + \ldots$ Subtracting the first equation from the second and putting

$$C'_p - Cp = \Delta Cp,\ a' - a = \alpha, \text{ and } b' - b = \beta,$$

we obtain

$$\Delta Cp = \Delta Cp_0 + \alpha t + \beta t^2 + \ldots$$

Combining this with the purely thermodynamic equation,

$$dL_F/dt = -dL_F/d(\Delta t_F) = -\Delta Cp,$$

and integrating, we obtain equation (85).

Strictly speaking, another term should be added to this expression to include the heat of compression of the liquid solvent from P to $P - \Pi$, since the operation of the engine produces liquid solvent at the latter pressure. In most cases this heat effect will be entirely negligible in comparison with the heat of fusion and this assumption is made in equation (85).

[24] The values of the constants for water are: L_{F_0} = 59.309 liter atmospheres, ΔCp_0 = 0.363 liter atmosphere per degree, V_0 = 0.01801 liter, a = 0.000014 liter; α, β, and b are negligible. For examples illustrating the application of equation (87) see Lewis, THIS JOURNAL, 30, 671 (1908).

Chamber **E**: Filled with a solution under the pressure P at its boiling point,[25] T_B. The mol fraction of the solvent is N_A and its partial vapor pressure, acting against piston **A**, is p ($= P$). The pure liquid solvent in cylinder **B** is under the osmotic pressure Π.

Chamber **E′**: Exactly as chamber **E** except that the mol fraction of the solvent is $N_A + dN_A$, the temperature (B. P.) is $T_B + dT_B$ and the osmotic pressure is $\Pi + d\Pi$. The vapor pressure is P.

$d\Pi$ in this instance is given by the expression

$$d\Pi = (\partial\Pi/\partial T)_N(\partial T_B/\partial N_A)_P dN_A + (\partial\Pi/\partial N_A)_T dN_A. \qquad (88)$$

To operate the engine, vaporize one mol of solvent from chamber **E′** by means of piston **AA′** and introduce simultaneously one mol of liquid solvent osmotically by means of piston **BB′**. The reverse process occurs in chamber **E**. The only work involved is that done by piston **BB′**, which is $Vd\Pi$. The heat absorbed at the higher temperature is the molecular heat of vaporization (L) of the pure liquid solvent under the pressure $p - \Pi$ to form vapor at the pressure p. We have therefore by the Second Law,

$$Vd\Pi = LdT_B/T_B, \qquad (89)$$

or

$$(\partial\Pi/\partial T_B) = L/VT_B. \qquad (90)$$

In this equation we can put

$$T_B = T_{B_0} + \Delta t_B$$

and obtain

$$d\Pi = Ld(\Delta t_B)/V(T_{B_0} + \Delta t_B), \qquad (91)$$

where Δt_B is the elevation of the boiling point in centigrade degrees and T_{B_0} is the boiling point of the pure solvent on the absolute scale.

The method of integration to be followed for this equation depends largely on the nature of the solvent, the equation of state of the vapor and the magnitude of T_{B_0} as compared with the critical temperature of the pure solvent. If the vapor of the solvent obeys the gas laws and T_{B_0} is considerably lower than the critical temperature, we could adopt a method of integration identical with that employed for the corresponding freezing point equation and would obtain an integrated expression perfectly analogous to equation (86). Consequently it will not be necessary to consider this case in further detail.

Vapor Pressure and Freezing-point Lowering (P = *const.*).—The problem may be stated as follows: How does the vapor pressure of the solvent from a solution vary with the temperature at which the solution is in equilibrium with the pure solid solvent? Now the vapor pressure from the solution and solid solvent are equal when the two are in equilibrium, consequently this question is the same as inquiring, How does the vapor pressure of the pure solid solvent vary with the temperature? and this relation has already been derived. It is equation (5) which we may write as follows (using T_F in place of T to indicate that we mean the absolute temperature of the freezing point of the solution):

---

[25] Note that the b. p. is here defined as the temperature at which the partial vapor pressure of the solvent is equal to the total pressure on the solution.

$$(\partial p/\partial T_I)_P = L_S/vT_F. \tag{92}$$

In this equation L_S is the molecular heat of sublimation of the pure solid solvent under the pressure P to form saturated vapor at the pressure p. dp is expressed by the equation

$$dp = (\partial p/\partial T)_N(\partial T_F \partial N_A)_P dN_A + (\partial p/\partial N_A)_P dN_A. \tag{93}$$

Let us integrate equation (92) for aqueous solutions. Assuming the perfect gas law for saturated water vapor below 0°, equation (92) may be written:

$$d\ln p = (L_S/R)dT/T^2. \tag{94}$$

Owing to the slight difference between the heat capacities of ice and its vapor, L_S will have such a small temperature coefficient that it may be regarded as constant without much error, even for large values of the freezing point lowering, Δt_F. Integrating equation (94) with this assumption we obtain

$$\ln p_0/p = (L_S/RT_0)\Delta t_F/T. \tag{95}$$

In this equation p is the vapor pressure of the solution at the absolute temperature of its freezing point T.

9. Summary and Conclusion.

1. A simplification of the cyclical process method of Carnot has been described, which reduces the cycle of necessary operations to a single step and allows the desired thermodynamic equation to be written down "by inspection." Not only does this result in an increased clearness and certainty as to the exact significance of the quantities appearing in the equation, but it also insures an entirely rigorous result because it is impossible to introduce into the process any assumption except the two laws of thermodynamics.

2. The use of this simplified process (embodied in what has been called the "Perfect Thermodynamic Engine") as the basis for the construction of a simple but entirely rigorous system of thermodynamic chemistry, is illustrated by applying it to the derivation of a number of fundamental relations.

3. The modified process possesses, to a higher degree, all of the advantages of the ordinary cyclical process with none of its disadvantages. The system of equations which it yields possesses all of the rigor of any of the analytic systems of thermodynamics with none of their abstruse conceptions and intricate, involved and long drawn-out derivations. By means of the perfect thermodynamic engine one can pass in a

single step from the Second Law of thermodynamics directly to the differential equation of the desired relation.

4. In connection with the application of the engine to the subject of chemical equilibrium, the following points have been brought out:

(*a*) Contrary to the statement of T. B. Robertson, the Mass Action Law is not an expression of the condition for equilibrium in a system whose equation of state is $p(v - d) = RT$.

(*b*) The derivation of the Law of the Constancy of the Solubility Product for a solute which dissociates in solution does not involve any assumption regarding the nature of the law which regulates the equilibrium between the undissociated molecules and their products of dissociation. Consequently the theoretical basis for the Solubility Product Law in the case of strong electrolytes is not destroyed by the fact that they do not obey the Mass Action Law, as inferred by Stieglitz.

5. It is shown that many of our equations which contain the van't Hoff i, involve an unnecessary number of assumptions and that each equation can be split up into two simpler equations, one involving only the ions, the other only the unionized molecules. The advantage of so doing is illustrated by a consideration of the experimental data of Noyes and Sammet on the solubility of orthonitrobenzoic acid.

URBANA, ILLINOIS, January 15, 1910.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS AND METALLIC SOLUTIONS: THE INTERACTION OF MIXED SALT SOLUTIONS AND LIQUID AMALGAMS (FIRST PAPER). A STUDY OF THE REACTION, $KHg_m + Na^{\cdot} \rightleftarrows K^{\cdot} + NaHg_n + (m-n)\,Hg$.

BY GEORGE MCPHAIL SMITH.

Received February 16, 1910.

It has previously been shown[1] that the alkali metals exist, in liquid mercurial solution, in the form of compounds of the general formula $MeHg_n$, containing only one atom of the amalgamated metal to the molecule. It has also been shown that a mixed solution, containing the chlorides of sodium and potassium, reacts readily with either sodium or potassium amalgam, with the rapid establishment of an equilibrium. The same has been found to be the case with sodium and rubidium, and sodium and caesium amalgams, when treated with the corresponding mixed solutions.[2]

The present paper is the outcome of a more detailed study of the first of these reactions. In subsequent investigations the alkali earth and other amalgams will be included.

---

[1] Ueber die relative Beständigkeit bzw. die Konstitution der verdünnten Amalgame der Alkali-bzw. Erdalkalimetalle. G. McP. Smith, *Z. anorg. Chem.*, 58, 381 (1908).

[2] *Loc. cit.*

Experimental Method.[1]—Approximately equimolal liquid sodium and potassium amalgams were prepared, and after filtration through chamois skin on the filter pump, they were at once filled into small sealing bottles, whose necks were then drawn into capillaries and sealed off. At intervals, the measured salt solutions, which had previously stood in the thermostat in stoppered Erlenmeyer flasks, were tared on a balance, and the desired quantities of amalgam were poured into them directly from the opened capillaries.[2] The flasks were then restoppered and put back into the thermostat, and the capillary necks of the sealing bottles were at once re-sealed. The reaction mixtures were agitated for a given time in the thermostat, after which they were taken out, one at a time, and treated as follows:

The aqueous solution was decanted and the amalgam was washed by passing it through a row of 5 beakers, each of which contained about 50 cc. of distilled water; the wash water was decanted each time before the amalgam was poured into the next beaker. In this way each amalgam was washed thoroughly in the course of 1 minute, and the chemical action of the wash water was negligible. The amalgams were finally decomposed with hydrochloric acid, and the extracts were analyzed. The experimental results are given in Table I.[3]

In the reversible reaction,[4]

$$\mathrm{KHg}_m + \mathrm{Na}^{\cdot} \rightleftarrows \mathrm{K}^{\cdot} + \mathrm{NaHg}_n + (m - n)\mathrm{Hg},$$

as carried out in these experiments, free mercury was present in such quantity that its concentration may be taken as constant. We have therefore a heterogeneous equilibrium of the second order, and if $[\mathrm{KHg}_m]$ and $[\mathrm{NaHg}_n]$, $[\mathrm{Na}^{\cdot}]$ and $[\mathrm{K}^{\cdot}]$ represent the relative molal concentrations at equilibrium, then the equilibrium constant,

$$\mathrm{K} = \frac{k_1}{k_2} = \frac{[\mathrm{KHg}_m] \times [\mathrm{Na}^{\cdot}]}{[\mathrm{NaHg}_n] \times [\mathrm{K}^{\cdot}]}.$$

---

[1] The mercury used in the preparation of the amalgams was purified by the ordinary methods, after which it was distilled under reduced pressure in a current of air. The salts were of Kahlbaum's manufacture, and the water employed was obtained by redistilling the distilled water of the laboratory, after having acidified it slightly with sulphuric acid.

[2] In all cases the interaction of the amalgam and the solvent-water was infinitesimal and it will be neglected in what follows.

[3] The five solutions employed in the first 10 experiments contained, respectively, 14.6150 g. NaCl + 9.3200 g. KCl, 7.3075 g. NaCl + 18.6400 g. KCl, 14.6150 g. NaCl + 4.6600 g. KCl, 3.6538 g. NaCl + 18.6400 g. KCl, and 7.3075 g. NaCl + 9.3200 g. KCl; they were made up, one after another, in the same 250 cc. measuring flask.

[4] The values of *m* and *n* are not known for the compounds in solution; they may have several values in the case of the crystalline compounds. For references to the literature, see *loc. cit.*

TABLE I.[1]

No.	t°.	Time. Min.	Molal concentration of mixed solution at start. NaCl.	KCl.	Volume of aqueous solution used. cc.	Metallic solution used.	Resulting amalgam gave on analysis NaCl+KCl.	K_2PtCl_6.	It therefore contained. K.	Na.	Which is equivalent to
1	24.0	40	1.00	0.50	100	50.5 g. K-amalgam	0.3485	0.2182	0.0350	0.1110	0.447% K
2	24.0	40	1.00	0.50	100	50.7 g. Na- "	0.3834	0.2034	0.0326	0.1265	0.290% Na
3	24.0	40	0.50	1.00	100	50.0 g. K- "	0.3593	0.5537	0.0888	0.0749	0.432% K
4	24.0	40	0.50	1.00	100	50.0 g. Na- "	0.4055	0.5540	0.0888	0.0929	0.290% Na
5	24.2	40	1.00	0.25	100	50.1 g. K- "	0.3324	0.1300	0.0208	0.1151	0.433% K
6	24.2	40	1.00	0.25	100	50.6 g. Na- "	0.3752	0.1131	0.0181	0.1340	0.289% Na
7	24.2	40	0.25	1.00	100	50.3 g. K- "	0.3482	0.7418	0.1190	0.0478	0.400% K
8	24.2	40	0.25	1.00	100	50.2 g. Na- "	0.4166	0.7838	0.1257	0.0697	0.287% Na
9	24.1	50	0.50	0.50	100	50.1 g. K- "	0.3345	0.3679	0.0590	0.0874	0.415% K
10	24.1	50	0.50	0.50	100	50.9 g. Na- "	0.3908	0.3577	0.0574	0.1108	0.289% Na
11	24.	30	2.00	2.00	50	50. g. K- "	0.3299	0.3173	0.0509	0.0918	......
12	24.	30	2.00	2.00	50	50. g. Na- "	0.3166	0.2846	0.0456	0.0904	......
13	17.	30	2.00	2.00	50	50. g. Li- "	0.0599	0.0540	0.0087	0.0171	......

[1] Samples of the amalgams were taken beforehand from the sealing bottles and analyzed. They gave: Na = 0.29 per cent. and K = 0.45 per cent., respectively.

Experiments 11 and 12 are taken from the paper already cited. In the case of Experiment 13 (which is taken from *Am. Chem. J.*, 37, 517 (1907)), the alcoholic filtrate from the potassium chloroplatinate was evaporated to dryness and the residue tested spectroscopically for lithium, of which not a trace could be detected.

Now, in the case of Experiments 1 and 7, for example,

$$\frac{\dfrac{0.0350}{39.10}[\mathrm{Na}^\cdot]_1}{\dfrac{0.1110}{23.00}[\mathrm{K}^\cdot]_1} = \mathrm{K} = \frac{\dfrac{0.1190}{39.10}[\mathrm{Na}^\cdot]_7}{\dfrac{0.0478}{23.00}[\mathrm{K}^\cdot]_7};$$

whence

$$\frac{]\mathrm{Na}^\cdot]_1}{[\mathrm{K}^\cdot]_1} \Big/ \frac{]\mathrm{Na}^\cdot]_7}{[\mathrm{K}^\cdot]_7} = 7.90.$$

And, starting with 100 cc. of solution and taking into account the changes in concentration during the reaction, we have at equilibrium in the case of these two experiments the molal relations:

$$\frac{(\mathrm{NaCl})_1}{(\mathrm{KCl})_1} \Big/ \frac{(\mathrm{NaCl})_7}{(\mathrm{KCl})_7} = \frac{\dfrac{2.3000 - 0.1110}{2.3000}}{\dfrac{1.9550 + 0.1887}{3.9100}} \Big/ \frac{\dfrac{0.5750 - 0.0478}{2.3000}}{\dfrac{3.9100 + 0.0813}{3.9100}} = 7\ 73.$$

From the approximate equation, 7 90 = 7 73, it follows roughly that

$$\frac{[\mathrm{Na}^\cdot]_1}{[\mathrm{K}^\cdot]_1} : \frac{[\mathrm{Na}^\cdot]_7}{[\mathrm{K}^\cdot]_7} = \frac{(\mathrm{NaCl})_1}{(\mathrm{KCl})_1} : \frac{(\mathrm{NaCl})_7}{(\mathrm{KCl})_7},$$

i. e., in mixed sodium and potassium chloride solutions, the ratios which exist between the relative ion concentrations of sodium and potassium in the different solutions are identical with those which exist between the relative molal concentrations of the two salts in the respective solutions. It is therefore permissible to substitute the latter values in the calculation of the equilibrium constant. The results are given in Table II:[1]

TABLE II.[2]

No.	Amalgam at start.	At equilibrium, $[\mathrm{KHg}_m] : [\mathrm{NaHg}_n]$.	From the relative molal concentrations at equilibrium, $[\mathrm{Na}^\cdot] . [\mathrm{K}^\cdot]$	Total molal concentration of mixed salt solution.	$\frac{[\mathrm{KHg}_m] \times [\mathrm{Na}^\cdot]}{[\mathrm{NaHg}_n] \times [\mathrm{K}^\cdot]}$.
1	Potassium...	15.64 : 84.36	0 9517 : 0 5482	1.50	0.322
2	Sodium......	13.12 : 86.83	1 0083 : 0.4916	1.50	0 311
3	Potassium...	41.08 : 58.92	0.4674 : 1.0325	1.50	0 316
4	Sodium......	36.00 : 64.00	0.5227 : 0.9773	1.50	0.315
5	Potassium...	9.03 : 90.97	0.9500 : 0.3000	1.25	0.314
6	Sodium......	7.22 : 92.78	1.0046 : 0 2454	1.25	0.318
7	Potassium...	59.42 : 40.58	0.2294 : 1.0207	1.25	0 329
8	Sodium......	51.49 : 48.51	0.2821 : 0.9678	1.25	0.309
9	Potassium...	28.43 : 71.57	0.4620 : 0.5380	1.00	0.341
10	Sodium......	23 35 : 76 65	0.5147 : 0.4853	1.00	0.323
11	Potassium...	24.61 : 75.39	1.9207 : 2.0798	4.00	0.302
12	Sodium......	22.90 : 77.10	2.0233 : 1.9762	4.00	0.303
13	Lithium.....	23.05 : 76.95	2.0 : 2.0	4.00	0.202

Mean value: $K = 0.315$

---

[1] **In the calculation of the molal concentrations at equilibrium, if sodium amalgam was started with, for example, then the potassium in the resulting amalgam came**

It is interesting to compare with the above the equilibrium constants calculated from previously published results[1] obtained in the action of mixed sodium and rubidium, and sodium and caesium chloride solutions upon sodium and rubidium, and sodium and caesium amalgams, respectively. In these cases the solutions were double molal in respect to each salt in the mixture, so that the concentration changes may be disregarded in calculating the values of the equilibrium constants. The results are given in Table III:

TABLE III.

No.	t°	Time Min	Amalgam at start	At equilibrium $[MeHg_m].[NaHg_n]$.	At start and at equilibrium $[Na^\cdot]$ $[Me^\cdot]$.	$\frac{[MeHg_m] \times [Na^\cdot]}{[NaHg_n] \times [Me^\cdot]}$.	Mean.
1	23	30	Rubidium	27.39 : 72.60	2.0 : 2.0	0.377	0.37
2	23	30	Sodium	26.35 : 73.64	2.0 : 2.0	0.358	
1	24	30	Caesium	32.95 : 67.05	2.0 : 2.0	0.491	0.48
2	24	30	Sodium	32.44 : 67.55	2.0 : 2.0	0.480	

From the foregoing we see that, in the case of the general reaction,

$$NaHg_n + (m-n)Hg + Me^\cdot \rightleftarrows MeHg_m + Na^\cdot,$$

the equilibrium constant is equal to 0.31, 0.37 and 0.48, respectively, when Me stands for K, Rb and Cs, in the order named.

Previous studies of the ionization of salts have led to the conclusion that at any definite concentration salts of the same ionic type have approximately the same degree of ionization. It has also been shown by experimental investigations that the degree of ionization of each salt in such a mixture as KCl + NaCl, in which there is a common ion, is the same as if that salt were alone present with an ion concentration equal to the sum of those of the two separate salts.[2] It therefore follows that, in such a mixed solution,

$$\frac{[Na^\cdot]}{[K^\cdot]} = \frac{\alpha_1(NaCl)}{\alpha_2(KCl)} = \frac{(NaCl)}{(KCl)}.$$

The present investigation offers, through an independent method, a

---

from the solution, and the equivalent amount of sodium must have entered the solution from the amalgam. The chemical action of the solvent water was negligible, as can be seen from the figures given in the last column of Table I.

[2] In regard to experiments 11, 12 and 13, see footnote under Table I. Experiment 13 is evidently unreliable, owing to the low lithium content of the amalgam at the start and to the different temperature. Of the first 10 experiments, the 9th is the least reliable. The source of error is suggested in the last column of Table I, where it is seen that the equivalent potassium content found was greater than that in experiment 7, which was performed 1 day earlier; owing to traces of oxidation in the meantime, the amalgam should have shown a lower potassium content. The mean value of K is not affected, however, if *both* experiments are left in the table.

[1] *Loc. cit.*

[2] For references to the literature on this subject, see A. A. Noyes and J. Johnston, THIS JOURNAL, 31, 987 (1909).

striking confirmation of the above conclusions, and, *moreover, it shows that they hold good even in the case of very concentrated solutions.*

URBANA, ILL., February, 1910.

CONCERNING THE CORRECTION OF THE APPARENT WEIGHT OF A SALT TO THE VACUUM STANDARD.

BY THEODORE W RICHARDS AND GREGORY P. BAXTER.

Received February 12, 1910

The tendency to adsorb gases possessed by finely divided carbon is well known, and there can be no question that other substances also possess, although to a much smaller degree, this same tendency. Therefore the possible effect of adsorbed gases upon the weights of the substances entering into very precise determinations, such as those concerning the atomic weights, is worthy of careful consideration. The idea is by no means new, for Marignac nearly seventy years ago investigated several salts with regard to the possibility of such adsorption, and found in most cases very slight, if any, evidence of an appreciable effect.[1] The topic has been recently revived by Guye and Zachariadès in a brief paper, in which are recorded, without details, a number of extraordinary results very different from those of Marignac.[2] The new investigators interpret their figures to mean that the error from this source is in many cases a serious one, rendering illusory the weighing of most powdered salts more accurately than to within one one-hundredth of one per cent.

The experiments of Guye and Zachariadès have been repeated, as far as potassium chloride is concerned, by Alexander Scott, with results confirming Marignac's rather than those of the new investigators. Scott was unable to find any important adsorptive effect, even in finely powdered potassium chloride.[3] His discussion of the matter seems to leave little need of further remark, except for the fact that Guye and Zachariadès specifically mention the recent Harvard investigations upon atomic weights, and their paper might convey to some the impression that these authors believe their results to concern the work at Harvard. It is very easy to show, however, upon the basis of the evidence in the paper, that, whether the interpretation by the two investigators at Geneva is correct or not, in any case their results can have no relation whatsoever to the Harvard work, and do not render necessary appreciable corrections in any of the Harvard investigations.

Guye and Zachariadès weighed successively in air and in vacuum a number of materials which, as they say, "were chosen especially as having served in the determinations of atomic weights in the chemical laboratory of Harvard College." These twenty-six salts were as follows: The nitrates of potassium and silver; the chlorides of potassium, sodium, magnesium, calcium, manganese, nickel, cobalt, iron, cadmium, barium, strontium, and silver; the bromides of potassium, sodium, zinc, barium, strontium, nickel, cobalt, and cadmium; the sulphates of copper and silver; the chlorate of potassium; the oxide of copper. Two of the substances, however—the chlorides of iron and nickel—have never been used as the basis of accurate work at Harvard. The authors conclude that the adsorptive effect "depend de la densité du sel, de l'hygroscopicité, et, à un haut degré des conditions de l'expérience, notamment de la structure physique du sel pesé." Thus, for example, fused potassium chloride in large pieces showed 5 milligrams of adsorption per 100 grams, in crystals 20 milligrams, in powder 32 milligrams. The other twenty-five substances seem to have been investigated in powdered form alone, and only one among them, namely, potassium nitrate, appeared to show as much adsorption as powdered potassium chloride.

---

[1] Marignac, *Oeuvres Completes*, 1, 44; also *Bibl. Univ.*, 46, 373 (1843).

[2] Guye and Zachariadès, *Compt. rend.*, 149, 593 (1909).

[3] Alexander Scott, *Proc. Chem. Soc.*, 25, 286 (1909).

Supposing for a moment that the figures just cited really represent adsorbed air, the quantity corresponding to fused material weighed in large pieces would be only enough to affect the atomic weight of potassium calculated from the molecular weight of potassium chloride, by an unimportant quantity, less than 0.004; and potassium chloride was one of the worst of all the substances investigated by Guye and Zachariadès. Hence, even according to their own showing, fused substances in large pieces may be weighed with considerable accuracy.

Now, of the substances in the list used in the Harvard determinations, all except five were fused and weighed in large pieces. This had been done not only because the expulsion of water from a fused salt is more certain than from a solid, but also because the possibility that the powders might adsorb air had been thought of very early in the prosecution of the Harvard researches. For example, in the case of barium bromide, the salt used in Experiments 4 and 13 was fused in a platinum crucible, and yet gave results for the atomic weight of barium and for the content of crystal water essentially identical with those of similar samples which had been merely heated at a high temperature without fusion, being thus in a highly subdivided, effloresced condition.[1] Two of the specimens of barium chloride (those used in Experiments 37 and 38[2]) were fused in a current of hydrochloric acid gas, but gave results for the atomic weight of barium essentially equal within the limit of error of experimentation to those from the unfused effloresced samples. In the later determinations of the atomic weights of other elements, the other substances mentioned by Guye and Zachariadès were all fused and weighed in large pieces except the five already alluded to. Of these five, nickel and cobalt bromides were weighed in the form of crystals of appreciable size, but Guye and Zachariadès found these substances even in a state of powder to show only a slight irregularity. Hence, they could not have been at fault. Copper oxide, another of the five, falls entirely out of consideration, partly because Guye found almost no suspicious effect in this case, and partly because if any air had been adsorbed by copper oxide it would have been determined along with the included nitrogen in the due course of the experiments upon this substance. Copper sulphate was indeed used in a finely powdered condition, but the weight of this substance did not enter into any of the finally accepted values for the atomic weight of copper. Hence the fourth of the unfused substances also falls out of consideration. Cobalt chloride also was used in an effloresced condition, but gave the same results for the atomic weight of cobalt as did the more compact cobalt bromide.

---

[1] Richards, *Z. anorg. Chem.*, 3, 470 (1893).

[2] Richards, *Ibid.*, 6, 121, 122 (1894).

Having thus shown that the results of the European experimenters do not at all concern the Harvard determinations, even if some powdered substances really occlude air, we may perhaps repeat a description of two series of experiments carried out within the last two years in the Harvard laboratory with finely divided substances not in the list given by Guye and Zachariadès. In recent experiments iodine pentoxide and powdered silver phosphate have been used as means of obtaining information concerning the atomic weights of iodine and phosphorus respectively Bearing in mind the possibility of this error in question (although at that time the paper of Guye and Zachariadès had not been published), Baxter and Tilley[1] and Baxter and Jones[2] carried out experiments with these two substances respectively. Iodine pentoxide had been made by double efflorescence from iodic acid through the compound $I_2O_5HIO_3$ and therefore must have been an extremely porous material with a surface comparable with that of charcoal. In two experiments with 25.8 grams of material, the air actually displaced by the pentoxide was found to be within about 0.0001 gram of that calculated from the density of the substance.

The description of these experiments is given below:

"Two weighing bottles were constructed with long, very well ground stoppers which terminated in stopcocks through which the tubes could be exhausted. These tubes were very closely of the same weight and of very nearly the same internal capacity. The tubes were first exhausted and compared in weight by substitution. Next they were filled with dry air and again weighed, the weighings being carried out with the stopcocks open." Both steps were then repeated with essentially the same results, the difference in the weight of air contained in the two tubes being found on the average to be 0.00014 gram, the counterpoise being slightly the larger.

---

[1] This Journal, 31, 214 (1909).

[2] *Proc. Amer. Acad.*, 45, 155 (1909). This Journal, 32, 298.

"Into one of the tubes was introduced 25.84 grams of carefully dried iodine pentoxide, and both tubes were completely exhausted. When the tube containing the pentoxide was warmed to about 150° no perceptible quantity of gas was evolved. After the difference in weight of the exhausted tubes had been determined, they were again filled with dry air and weighed, and the process of exhausting the tubes and filling them with air was repeated." The difference between the weight of air admitted to the two tubes now averaged 0.00651 gram, corrected to 19° and 758 mm. Subtracting the difference found for the empty tubes (0.00014 gram), the quantity 0.00637 gram is found as the weight of air displaced by the powder, whereas the value calculated from the density of the solid (4.799[1]) is 0 00649. Thus the amount of air adsorbed by nearly twenty-six grams of the very finely subdivided, effloresced iodine pentoxide was only a trifle more than 0.1 milligram—a quantity scarcely greater than the probable error of experiment. In this case the usual method of calculating the correction to the vacuum standard yields a possible error of only 1 in 200,000.

Similar experiments have been made with *precipitated* and dried silver phosphate by Baxter and Jones with similar results.

"In two experiments, when air was admitted, after exhaustion the counterpoise gained 0.00028 and 0.00021 gram respectively (average 0.00025), more than the tube which was later to contain the silver phosphate. After 22.69 grams of pure dry silver phosphate had been placed in the tube, the tube and its counterpoise were exhausted and the difference in weight determined. When dry air at 25° and 766 mm. was admitted to both the tube containing the silver phosphate and the counterpoise, the counterpoise gained 0.00443 gram more than the tube. Therefore the air displaced by the silver phosphate was 0.00443 — 0.00025 = 0.00418 gram. Since 22.69 grams of silver phosphate of density 6.37[2] have a volume of 3.56 cc., the volume of pure air displaced at 25° and 766 mm. should weigh 0.00425 gram.

"The experiment was then repeated. After the air had been exhausted from the tube and its counterpoise, the tube containing the silver phosphate was heated gently. No gas was evolved. The tube and its counterpoise were then weighed by substitution. When dry air at 24.5° and 767 mm. was admitted to both, the counterpoise gained 0.00445 gram more than the tube containing the silver phosphate. Therefore the air displaced by the silver phosphate was 0.00445 — 0.00025 =

---

[1] Baxter and Tilley, THIS JOURNAL, 31, 213 (1909).

[2] Baxter and Jones, *Proc. Amer. Acad.*, 45, 155 (1909).

0.00420 gram, whereas the weight of air displaced, calculated from the density of the salt, is 0.00426 gram.

"The agreement between the experimental results and those calculated from the density of silver phosphate on the assumption that no adsorption takes place is close enough to show that no significant amount of adsorption occurs."

Furthermore, in many cases dried precipitates of silver halides have been weighed both before and after fusion, and, while in some cases the loss has amounted to 0.01 per cent., owing to moisture retained by the dried salt, in many cases the loss in weight has been very slight indeed, showing that the great diminution in surface is without effect upon the apparent weight. This was especially the case in the recent investigations upon the atomic weights of bromine and lithium, wherein silver bromide and chloride dried for a long time at 180° and 250°, respectively, lost sometimes not more than 1 part in 100,000 on fusion. Even this almost negligible loss was probably due to traces of water imprisoned in the unfused substance.[1]

When with these results we rank the similar results of Scott with potassium chloride, one cannot but believe that many substances at any rate adsorb so little air as not to be greatly affected as to their weights thereby, at least when the solids are weighed in any ordinary state of subdivision.

One other case, that of sublimed ammonium chloride, may receive passing mention. This salt seems to exhibit a slight tendency in the opposite direction, as it gains somewhat more weight in vacuum than corresponds to the calculated correction. According to the concordant results of Marignac, Stas, and Richards and Köthner and Tiede[2] the salt gains 0.00080 gram per gram when the air is exhausted, whereas the best value for the density of transparent ammonium chloride (1.525) corresponds to a gain of 0.000793—a result but very slightly less than the observed value.

Sublimed ammonium chloride is, however, a peculiar substance because, on cooling, it suffers transition into a denser form, causing the crystals to be permeated with pores of molecular fineness. The porosity of the solid renders difficult the determination of its true bulk, upon which depends the correction to the vacuum standard. Some of the interstices would undoubtedly fill with air, while others might not; and none of them would probably fill with a liquid. This would account for Stas's uncertainty about the specific gravity of the salt, and for the various interpretations which have been put upon the results. Hence ammonium chloride, also, is probably not fundamentally abnormal.

---

[1] Baxter, THIS JOURNAL, 28, 1332 (1906). Richards and Willard, *Ibid.*, 32, 29 (1910).

[2] Marignac, *loc. cit.*; Stas, *Untersuchungen*, Aronstein's translation, p. 56 (1867); Richards, Köthner, and Tiede, THIS JOURNAL, 31, 7 (1909).

The details given in the recent paper by the Geneva experimenters are so meagre that an explanation of their unprecedented results can hardly be attempted. They make no mention of the degree of purity of the salts or the precautions taken in drying them before the experiment. This is, however, a matter of great importance, for the preparation of many of these salts in a pure state, free from water, is a very difficult matter; indeed it is almost impossible to obtain some of them in a powdered form and yet entirely anhydrous. Hence, as they weighed the salts first in air and then in a vacuum, a loss of weight may have been due simply to loss of moisture, as Scott has pointed out in the criticism already quoted. If the salts had been weighed first in vacuum and then in air, the presence of a trace of moisture could have had no effect on the result. Baxter and Tilley, and Baxter and Jones employed this method, as did also Scott.

After the present paper was sent to the press, another paper by the experimenters at Geneva has come to our notice.[1] In it the magnitudes of all the assumed abnormalities have been somewhat changed, and the corrections have apparently been given the opposite sign in every case. Criticism of this unexpected development will not be attempted here; it is enough to say that the arguments brought forward above concerning the Harvard results are not in any wise affected by the changes. No hasty investigation can throw light upon any matter of this kind. The details, both as regard purity of materials and precautions in treatment, must be as thoroughly worked out as in a most careful determination of an atomic weight in order that the work may have any significance.

The contents of this paper may be briefly summarized as follows: First, the possible adsorption of gases by solids had not been overlooked in the Harvard investigations; secondly, even if the conclusions of Guye and Zachariadès hold under their conditions, these conclusions do not essentially affect the determinations of atomic weights conducted in the chemical laboratory of Harvard College; and thirdly, in the light of other careful work carried out, not only in this laboratory but also by Scott, it seems improbable that either of the interpretations by Guye and Zachariadès of their own results is free from fault.

CAMBRIDGE, MASS., February 9, 1910.

---

[1] Guye and Zachariadès, *Compt. rend.*, 149, 1122 (December, 1909).

[Contributions from the Laboratory of Physical Chemistry of the University of Illinois.]

THE ATOMIC WEIGHT OF HYDROGEN.

By Grinnell Jones.

Received February 2, 1910.

In 1908, W. A. Noyes[1] published a table giving the results of all the chemical determinations of the atomic weight of hydrogen, and showed by a careful criticism and comparison that the only data obtained by the chemical methods which need to be considered in selecting the most probable value are those published by Morley[2] in 1895, and by Noyes[3] in 1907.

Noyes states that "densities of gases corrected to the condition of an ideal gas by the method of D. Berthelot may be considered as direct comparisons with oxygen, and molecular and atomic weights calculated from these densities should be included with those determined by chemical methods." But he does not add the results obtained by these physico-chemical methods to his table or discuss their value in selecting the most probable atomic weight of hydrogen.

The object of the present paper is to collect the results which have been obtained by the physico-chemical methods and compare them with the result obtained by the chemical methods. In a few cases the results have been recalculated with the use of the most reliable densities of hydrogen and oxygen at present available, namely, those of Morley. In a few cases other minor corrections have been made and the calculations carried out to one more decimal.

D. Berthelot's[4] "method of limiting densities" for calculating exact molecular weights is based on the deduction from the kinetic theory of gases that all gases approach the ideal gas as the pressure is reduced, and that at infinitesimal pressure, Avogadro's hypothesis is strictly true. This may be expressed in more mathematical language as follows: The limit of the ratio of the densities of two gases as the pressure approaches zero is equal to the ratio of the molecular weights of the gases. Berthelot shows in a very simple manner that these relationships may be expressed by

$$M/M' = (1 - A_0^1)D/(1 - A'^1_0)D',$$

where M and M′ are the molecular weights of the two gases, D and D′ are the densities under normal conditions, and A_0^1 and A'^1_0 are the mean coefficients of the deviation from Boyle's law per atmosphere at

---

[1] This Journal, 30, 7 (1908). See also discussion of this subject by Brauner in Abegg's "Handbuch der anorganische Chemie," Vol. II, Part 1, page 9.

[2] Morley, "Smithsonian Contributions to Knowledge," 1895.

[3] This Journal, 29, 1718 (1907).

[4] *J. physique* (3), 8, 263 (1899).

0°, between zero pressure and one atmosphere. This coefficient is defined by the relation

$$d(\mathrm{PV})/\mathrm{PV}d\mathrm{P} = -\mathrm{A},$$

which gives the value of A at any pressure, P, and corresponding volume, V. The negative sign has been inserted simply for convenience, since without this convention A would be negative for all gases except hydrogen and helium, under normal conditions. It has been shown experimentally by Rayleigh[1] and Chappuis,[2] and theoretically by Berthelot,[3] that for the gases formerly called "permanent" the value of A does not vary with the pressure by an appreciable amount below two atmospheres pressure. Therefore, the value A_0^1 can be taken equal to the value of this coefficient as determined experimentally by Leduc and Sacerdote,[4] Rayleigh,[5] Chappuis,[6] Berthelot,[7] and Jacquerod and Scheuer[8] at pressures up to two atmospheres. Although this procedure necessarily involves an extrapolation, the kinetic theory of gases indicates that this extrapolation is a comparatively safe one.

The following table gives the values for A_0^1 and $1-A_0^1$ for hydrogen and oxygen found by different experimenters:

	Hydrogen		Oxygen	
	A_0^1	$1-A_0^1$	A_0^1	$1-A_0^1$
Leduc and Sacerdote	—0 00064	1 00064	0 00076	0 99924
Rayleigh	—0 00053	1 00053	0.00094	0 99906
Chappuis	—0.00058	1 00058	..	.
Jacquerod and Scheuer	—0 00052	1.00052	0.00097	0 99903
Berthelot	—0 00060	1 00060	0.00085	0 99915

The last three experimenters worked at 0°. Rayleigh worked at about 11°, finding at this temperature —0 00052 for hydrogen and +0 00076 for oxygen. He corrected his results to 0° by means of a formula proposed by Berthelot[9] after a careful study of Chappuis' excellent experimental results on this subject. Leduc and Sacerdote found A for oxygen at 16° to be +0.00061, and then corrected this result to 0° by means of a complex empirical formula burdened with numerous empirical constants, obtaining +0.00076. I have made this correction by means of Berthelot's formula and obtained +0.00083. The necessity for applying this temperature correction of course diminishes the reliability of these results. Fortunately, we have compressibility measurements made at 0°. In the case of hydrogen, the value of A varies so little with the temperature that the method of applying the correction is unimportant.

---

[1] *Phil. Trans.*, 198A, 417 (1902); 204A, 351 (1905).

[2] Chappuis, "Nouvelles Études sur les Thermomètres a Gaz." Travaux et Mémoires du Bureau International des Poids et Mesures, Vol. XIII.

[3] Berthelot, *loc. cit.* Also "Sur les Thermomètres a Gaz." Travaux et Mémoires du Bureau International des Poids et Mesures, Vol. XIII.

[4] Leduc and Sacerdote, *Compt. rend.*, 125, 297 (1897). Leduc, *J. physique* (3), 7, 5 (1898).

[5] Rayleigh, *loc. cit.*

[6] Chappuis, *loc cit.*

[7] Berthelot, *Compt. rend.*, 145, 182 (1907).

[8] Jacquerod and Scheuer, *Compt. rend.*, 140, 1384 (1905); *Mem. Soc. Phys. Hist. Nat. Geneve*, 35, 659 (1908).

[9] Berthelot, *Sur les Thermomètres a Gaz. l. c.*

Leduc and Sacerdote did not use their data to calculate atomic weights by the method of limiting densities. When Berthelot first proposed this method, he calculated from these measurements of the compressibility and Leduc's measurements of the densities of hydrogen and oxygen that the atomic weight of hydrogen is 1.0072. There can, however, be little doubt that the density measurements of Morley are the most accurate at present available.[1] Berthelot[2] has recently repeated this calculation, using Morley's densities, and obtained 1.0077 (1.00768). If we correct Leduc and Sacerdote's measurement of the compressibility of oxygen to 0° by Berthelot's method, this result becomes 1.00775, which is probably the best result which can be derived from these measurements.

Similarly, Rayleigh used his own values for the densities and obtained 1.0086, which he admitted to be too high. He did not combine his excellent compressibility measurements with Morley's densities, but when this is done we obtain 1.00775.

Jacquerod and Scheuer used Morley's value for the density, so their result stands, 1.00777.

Berthelot has not yet used his compressibility measurements to calculate atomic weights so far as I have been able to find. His measurements lead to 1.00773.

Unfortunately, Chappuis did not make any experiments with oxygen. His work on hydrogen is very thorough, and is a very valuable confirmation of the calculations made above.

Guye's[3] method for the reduction of the critical constants is based on van der Waals' equation, the constants a and b being calculated from the critical constants. Unfortunately, van der Waals' equation is only an approximation, and for this reason Guye finds it necessary to insert in his formula another term involving the critical pressure and an arbitrary empirical constant. For gases whose critical temperature is above 0°, he finds it necessary to adopt a different and more complex method, involving two empirical constants. Although the method gives results in good agreement with those obtained by chemical methods in most cases, it hardly deserves as serious consideration as the chemical method or Berthelot's method of limiting densities in selecting the most probable value of an atomic weight. Guye,[1] using Morley's values for the densities, and Dewar's values for the critical constants of hydrogen ($Tc = 32$, $Pc = 19.4$), and Olszewski's values for the critical constants of oxygen, has calculated the atomic weight of hydrogen to be 1 00765. If we substitute Olszewski's[2] recent data for the critical constants of hydrogen ($Tc = 32°$, $Pc = 13.4$ to 15), we obtain 1.0078.

---

[1] See Guye, THIS JOURNAL, 30, 143 (1908).

[2] Berthelot, *Compt. rend.*, 144, 78 (1907).

[3] *J. chim. phys.*, 3, 321 (1905), and many other articles.

Berthelot[3] has criticized Guye's method on theoretical and mathematical grounds and proposed a method of his own for the calculation of the correction to the ratio of the densities by the help of the critical constants. This method is based upon a modified form of van der Waals' equation, which Berthelot[4] proposed after a careful consideration of Chappuis' wonderful experimental work on hydrogen, nitrogen, and carbon dioxide under conditions not very far removed from normal. Berthelot calls this method the method of "indirect limiting density," but it would seem to be more appropriate to call it Berthelot's method of "critical constants," since the critical constants are used instead of the compressibility as in Berthelot's "direct limiting density" method. Berthelot, using the critical constants of Wroblewski, which have recently been confirmed by Olszewski, has calculated the atomic weight of hydrogen to be 1.0076. The critical pressure of hydrogen is not known with sufficient accuracy to determine the fourth decimal place by this method, even if we assume that the formula is exact.

Leduc,[5] using his method of molecular volumes, calculates the correction which must be applied to the ratio of the densities of gases by means of a very complex formula containing six empirical constants. Although a result obtained in this way has very little value as proof of an exact atomic weight, Leduc's result is included for the sake of completeness and to show that its evidence does not conflict. Leduc, using his own values for the densities, obtains $H = 1.0073$. If, however, we combine Morley's values for densities with Leduc's correcting factor, we obtain $H = 1.00765$.

In the following table the final corrected results are collected. The name before each number does not necessarily mean that the number can be found in the literature in an article published by the given author. In the case of the method of limiting densities, the numbers have been calculated by Berthelot's method from the experimental data on compressibility, found by each authority named. In the case of the other physico-chemical methods, the name indicates the method of calculation used. All the results are derived from Morley's values for the densities (except, of course, the results of the chemical methods which are independent of these results):

---

[1] *Compt. rend.*, 138, 1213 (1904).

[2] *Ann. chim. phys.* (8), 8, 193 (1906).

[3] *Compt. rend.*, 144, 78, 194 (1907).

[4] *Sur les Thermometres a Gaz. loc. cit.*; also *Compt. rend.*, 144, 76, 194 (1907).

[5] *Compt. rend.*, 148, 407, 548 (1909).

THE ATOMIC WEIGHT OF HYDROGEN.

Chemical methods:	
Morley	1.00762
Noyes	1.00787
Mean of chemical methods	1.00775
Method of limiting density:	
Leduc and Sacerdote	1.00775
Rayleigh	1.00775
Jacquerod and Scheuer	1.00777
Berthelot	1.00773
Mean	1.00775
Method of critical constants:	
Guye (Dewar)	1.00765
Guye (Olszewski)	1.0078
Berthelot (Wroblewski, Olszewski)	1.0076
Method of molecular volumes:	
Leduc	1.00765

All of the physico-chemical results fall within the limits of the best chemical data. The wonderful agreement of the results obtained by the method of limiting density shows that the compressibility data are probably very accurate, and that the largest source of error in these results is probably Morley's density of hydrogen.

The conclusion drawn by Noyes from the chemical methods that 1.00775 is the most probable value for the atomic weight of hydrogen, is confirmed in a very striking manner by the method of limiting densities, which, as has been pointed out, is the most reliable of the physico-chemical methods.

URBANA, ILL., February 2, 1910

THULIUM.

(PRELIMINARY ANNOUNCEMENT.)

BY C. JAMES.

Received February 26, 1910.

The writer has obtained about 250 grams of the bromate of Cleve's thulium by the continued fractionation of the rare earth bromates more soluble than erbium.

This earth, discovered in 1879, has hitherto never been obtained in a pure condition. It is very rare, and comparatively large amounts of the ytterbiums are obtained during its preparation.

To obtain this quantity of material about 200 kilos of euxenite, ytterspar, gadolinite, fergusonite and yttrotitanite were employed; and in addition the yttrium earths derived from large quantities of monazite, supplied by the Welsbach Light Company through the courtesy of Dr. H. S. Miner, to whom many thanks are due.

Thulium bromate is more soluble than erbium bromate, but less soluble than the corresponding compound of ytterbium.

Thulium salts are of a pale bluish green color, best seen in artificial light. However, this tint is very readily destroyed by minute amounts of erbium, the solution becoming first yellowish green, then yellow, colorless, and lastly pink as the erbium content increases.

The material is still undergoing fractionation so as to make sure of the non-complexity of this element.

In addition to the above, it may be as well to state that the more soluble portions are being carefully studied, since the most soluble fractions are colored pale yellowish green when in solution while the intermediate fractions between these and thulium are colorless.

It is expected that early in May the determination of the atomic weight will have been completed and a study of the compounds commenced. All these fractions are being examined by means of a quartz spectrograph and Sir William Crookes has kindly offered to investigate the spark spectra of thulium and erbium with the unequaled instruments at his disposal. This latter element has also been obtained in a high state of purity.

NEW HAMPSHIRE COLLEGE, DURHAM, N. H.,
February 15, 1910

THE MARSH TEST AND EXCESS POTENTIAL.

(FIRST PAPER.[1])

THE QUANTITATIVE DETERMINATION OF ARSENIC.

BY W. D. HARKINS.

Received May 14. 1909.

Introductory.

The most widely used method for the determination of small quantities of arsenic is the separation as arsine suggested by Marsh,[2] together with the decomposition of this gas in a heated glass tube as recommended by Liebig.[3] An excellent review of the history of the development of this method has been given by Lockemann.[4]

---

[1] Presented at the New York meeting of the American Chemical Society, December 28, 1906, and in part at the December, 1905, meeting of the Stanford Chemical Society.

[2] *Ann.*, 23, 207 (1837).

[3] *Ibid.*, p. 217.

[4] *Z. angew. Chem.*, 18, 416 (1905).

In the year 1902 the writer attempted to utilize the Marsh method for the direct determination of the arsenic contained in the acid extracts from soils, but found that the amounts of arsenic recovered were entirely too small. This was explained by the work of Parsons and Stewart[1] and other investigators[2] as due to the retentive effect of the iron present in the solution. According to Headden and Sadler[3] a successful determination by this method can be made only in the absence of iron, copper, platinum and their salts.

In spite of the exidence cited above, and that of other observers,[4] A. H. Allen[5] recommends that zinc should always contain a certain amount of iron to insure a regular evolution of hydrogen, and Gautier[6] advises that platinic chloride be added in order to make the zinc active. Even in what he claims to be his most delicate method,[7] he precipitates the arsenic together with ferric hydroxide and adds the solution of this precipitate, containing about 0 1 gram of iron, directly to the Marsh generator.

Retention of Arsenic by Iron and Other Metals.

In view of these facts it was thought advisable to repeat a portion of the work of Parsons and Stewart. The experiments confirmed their work in every respect, showing that approximately the same percentages of arsenic were held back by the iron as those given in their paper. The results obtained, together with a few of the data given by Parsons and Stewart, are appended in Table I:

TABLE I – RETENTION OF ARSENIC BY IRON.

Wt Zn.	Reagent	Wt Iron.	Arsenic		Per cent Found	Time. Hrs
			Taken	Found		
35 g.	H_2SO_4	0 160 g.	1.88	1.00	53	6
35	HCl	0 400	1.88	0 72	38	5
35	H_2SO_4	7 000	1.88	0.30	16	6
35	HCl	7 $FeCl_2$	1.88	0 25	13	6
35	H_2SO_4	0.150	0.80	0.52	65	6
35	H_2SO_4	0.150	0.93	0 55	59	4
		Parsons and Stewart.				
30		0 060	5 00	3 45	69	
30		0.300	5 00	2.70	54	
30		1.500	5.00	2.95	59	
30		6.000	5.00	1.60	32	

[1] THIS JOURNAL, **24**, 1005 (1902).

[2] Wöhler, *Ann.*, **23**, 217 and 223 (1837). Santermeister, *Chem.-Ztg*, **15**, 1021. J. Thiele, *Chem. News*, **67**, 125 (1893).

[3] *Am. Chem. J.*, **7**, 341.

[4] O. Hehner, *J. Chem. Soc. Ind.*, **20**, 194 and 200. Chapman, "Reports of the Royal Commission on Arsenical Poisoning," Vol. II, page 84.

[5] *J. Soc. Chem. Ind.*, **21**, 94 (1902).

[6] *Bull. soc. chim.*, **27**, 20–21, 1030–34 (1902). *Ann. chim. phys.* (5), **8**, 384 (1876).

[7] *Compt. rend.*, **137**, 158–63. *Bull. soc. chim.* (3), **29**, 859–863.

In addition to these results it was found that mercury, platinum, silver, palladium, nickel, cobalt, and their salts were injurious in their action, particularly mercury,[1] and that copper is injurious when added in large amounts as copper sulphate to the solution. The following table gives the results of four experiments upon copper.

TABLE II

Grams Zn	Grams Cu	Time Hrs	Arsenic Found Mg	Arsenic Added Mg
35	0.037	6	1.88	1.88
35	0.184	6	1.80	1.88
35	0.368	6	1.79	1.88
35	7.000	6	0.22	1.88

The addition of tin, bismuth, cadmium, lead, or their salts to the generator did not cause the retention of any arsenic, except in cases where their addition diminished the rapidity with which the zinc was dissolved.

The Separation of Arsenic from Iron by Heating the Marsh Generator.

It was observed early in the course of the experiments upon the retention of arsenic by iron, that even after the arsenic had almost stopped depositing in the tube, a sudden increase in the rapidity of the evolution of hydrogen would cause a considerable evolution of arsine. It was found impossible to obtain a quantitative separation by merely increasing the rate of evolution of the hydrogen, but, when the generator was heated to 100° in a water bath, excellent results were obtained. The apparatus is shown in Fig. 1.

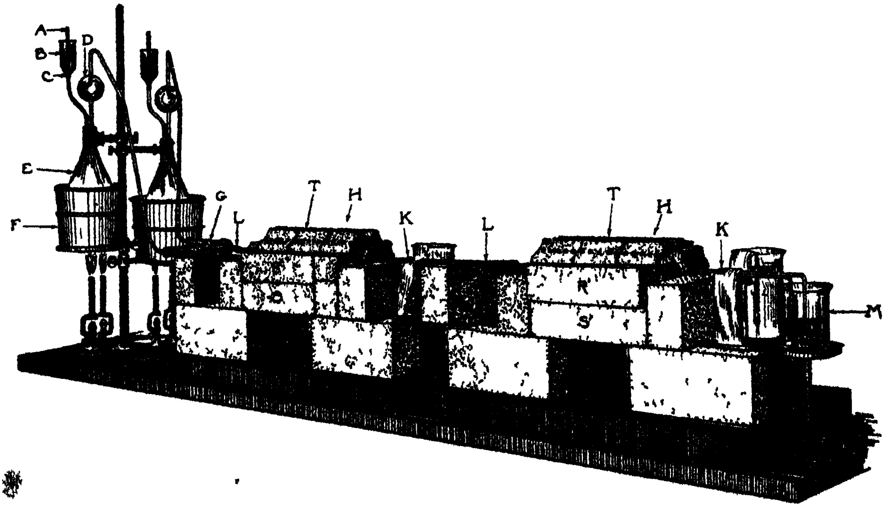


Fig. 1.—Apparatus for the determination of arsenic.

---

[1] Wm. Thompson, *Chem. News*, 85, 173 (1901) and 86, 179 (1902). The action of the mercury is very different from that of the other injurious metals, since it lessens the rapidity of the solution of the zinc, while the other metals increase its rate of solu-

At *A* is connected an apparatus giving arsenic-free hydrogen, which is passed through the tube *A C* into the flask *E*, until the air in the apparatus is completely displaced. Then, by turning *A*, acid may be dropped into the flask upon the zinc. The arsine and hydrogen pass through a Kjeldahl bulb, *D*, and a drying tube of calcium chloride, *G*, into a Jena hard-glass tube which lies in the fire-brick furnace *R S*. A second tube and furnace are always used to test the completeness of the decomposition of the arsine. The tubes are cooled at *K* by a strip of wet filter paper, or better by water flowing through a metal trough. Except where large quantities were determined, the glass tube was four millimeters in internal diameter, but drawn out to a smaller diameter where the arsenic was to be deposited. For all amounts greater than one-half milligram, the tube was enlarged to a bulb at *K*. The tube was finally cut at *a* and *c* (Fig. 2) and wiped by a slightly moist cloth. The tube was then left in the balance case for a considerable time and weighed by substitution against a tube of the same size and shape and made from the same glass. The arsenic was then dissolved in nitric acid and the tube washed with distilled water, dried in air, and finally weighed exactly as before on a balance sensitive to 0.005 mg. To avoid errors in a weighing care must be taken to deposit the arsenic in as small a tube as possible. Most of the weighings were made at a high altitude, where the air is light and very dry. The tubes were handled by forceps with flexible platinum tips, and by platinum wires.

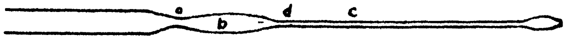


Fig. 2.

For each analysis about forty grams of arsenic-free zinc were used. The determination was begun by dropping a cold hydrochloric acid solution of the arsenic at such a rate that all of the arsenic was added during a period of one-half hour. Then the solution was heated gradually by boiling, and when the action had subsided somewhat more hydrochloric acid (sp. gr. 1.1) was added,[1] 100 to 150 cc. of acid in all. Finally 25

[1] All of the methods for the purification of hydrochloric acid described in chemical literature were tried, and in addition some others which seemed to give promise of success. The only method which always gave perfectly arsenic-free hydrochloric acid was a modification of that described by Otto ("Ausmittelung der Gifte," p. 159). Either mercuric chloride or copper sulphate was added to hydrochloric acid of a density of 1.10, in the proportion of ten to twenty grams to six liters of acid. Hydrogen sulphide was then passed until the salts were completely precipitated as sulphides, the bottle stoppered, and the solution allowed to stand for four or five days. At the end of this time it was filtered and the filtrate distilled, the first quarter of the distillate being rejected.

cc. of concentrated sulphuric acid mixed with 25 cc. of water were added to the generator. At once, when all the zinc was dissolved, the burners of the fire-brick furnaces were extinguished, the tile lifted from the furnaces, and the tubes cooled as quickly as possible. If this is not done, air will draw back into the apparatus and water vapor be formed and condensed, thus spoiling the determination. In cases where time is an object, the generator should be heated from the beginning.

After a series of preliminary experiments the results given in Table III were obtained:

TABLE III.—EFFECT OF HEAT UPON THE RETENTION OF ARSENIC BY IRON.

Wt. zinc. Grams.	Time cold. Hours.	Iron added Gram.	Time 100°. Hours.	Arsenic found. Milligrams.	Arsenic taken. Milligrams.
35	8	0.0	0.0	1.87	1.88
30	5	0.0	0.0	1.84	1.88
30	5	0.075	1.5	1.85	1.88
50	1	0.400	6.5	1.82	1.88
30	3.5	0.300	4.5	1.87	1.88
35	4.0	0.160	2.5	1.87	1.88
40	1.0	0.160	3.0	1.86	1.88
40	0.5	0.400	2.5	1.86	1.88
40	0.5	0.400	4.0	1.89	1.88
40	0.5	0.400	4.0	1.90	1.88
40		0.400	2.0	1.80	1.88
40		0.400	2.0	3.76	3.76
40		1.000	2.0	3.70	3.76

A comparison of these results with those given in Table I shows that heating the generator practically doubles the amount of arsenic reduced. It is evident that the directions which usually accompany the description of the Marsh test, namely that the generator be kept cold, are certainly erroneous and just the opposite of the best procedure. The directions should say that the concentration of the sulphuric acid present should be kept small near the beginning of the determination. For this reason hydrochloric acid is the better acid to use at first. The addition of moderately concentrated (1 : 1) sulphuric acid toward the end of the test improves the results, and the acid does not prove injurious by a resulting reduction.

In several cases, where the arsenic was deposited with extreme rapidity, a part of the mirror was a dark brick-red. This was not due to selenium, since the latter metal was not present. It is possible that this red substance was an allotropic modification of arsenic. In these experiments a white crystalline deposit was often obtained between the gas flame and the arsenic mirror. It is much less volatile than the arsenic, and can easily be separated from the latter by cutting the tube at the proper point. In appearance it is somewhat similar to that obtained when aluminium is used in the place of zinc in the generating flask. These deposits will be collected until a sufficient amount is obtained for the determination of the composition of the crystals.

The Separation of Arsenic by the Addition of Salts to the Generator.

The purest zinc which can be purchased dissolves in pure sulphuric acid with extreme slowness. If the salt of a metal which lies lower in the electromotive series is added to the acid it is found that in almost all cases the metal precipitates upon the zinc, but in such a way as to leave a part of the zinc surface in contact with the solution. If the metal thus precipitated has a lower excess potential than the zinc, which is the case with all of the metals considered in this paper with the exception of mercury, it would be expected that hydrogen would be liberated more easily from the surface of the second metal. In such cases we find that the zinc dissolves more rapidly than before, except that when salts of iron are added without vigorous stirring a considerable time often elapses before its effect is perceptible.

We may assume that the mechanism of solution of the zinc is now as follows: positively charged zinc ions pass from the surface of the zinc into the solution, and positive hydrogen ions are deposited upon the surface of the other metal, which for convenience we may consider as platinum. Gaseous hydrogen soon escapes from the surface of the platinum, and the mechanism of the reaction is the same as though the zinc and the platinum were connected by a wire, lying outside the solution. The system is a galvanic cell in which the zinc is the negative pole. So far as the platinum is concerned, however, the conditions are practically the same as if it were the cathode in an electrolytic cell containing sulphuric acid as an electrolyte. With such a system the reduction may take place either at the surface of the zinc or of the platinum electrode. If at the latter surface only, we have a case of cathodic reduction similar to that described by Tafel[1] or by Haber,[2] except that the depolarizer is itself a weak electrolyte in the case under investigation.[3] If we assume that the reduction takes place upon the surface of the cathodic metal, the reducing power should be related in some way to the value of the cathode potential. This potential depends upon the current density, the concentration of the oxide of arsenic, and the value of the excess potential for the particular metal. The value of the cathode potential (E) is given by the equation of Haber[4] for the case where no free hydrogen is liberated,

---

[1] *Z. physik. Chem.*, 34, 197 (1900).

[2] *Ibid.*, 32, 193 and 271 (1901); 47, 257 (1904).

[3] Luther and Schilow, *Z. physik. Chem.*, 46, 777 (1900). This, of course, makes *possible* the direct electrolytic separation of arsenic, provided that the conditions are favorable. That arsenic is precipitated as a metal when the reducing action in the generator is small is well known (Parsons and Stewart, *loc. cit.*).

[4] *Z. physik. Chem.*, 47, 259 (1904).

$$E = x(\mathrm{RT}/n \ln I/C_{\mathrm{M}}C_{\mathrm{H}^{\cdot}} - \mathrm{const.}),$$

where I is the current density; C_M, the concentration of the substance to be reduced; $C_{H^{\cdot}}$, the concentration of the hydrogen ion; x is a number greater than one, whose value depends upon the value of the excess potential for the metal, and the subtractive constant represents the catalytic influence of the cathode metal upon the reduction in question.

From a theoretical standpoint, the simplest case for investigation would have been the reduction of the oxide of arsenic in an electrolytic cell,[1] with a high concentration of arsenic, vigorous stirring, and a relatively low current density. However, since the work was undertaken at the beginning in order to increase the accuracy of the quantitative determination of small (but still weighable) amounts of arsenic by the ordinary Marsh method, the most favorable conditions for the proof of the theory were not chosen, but instead a much more complicated system was used in which the concentration of the oxide of arsenic was low, and the current density large. Of the factors in the determination of the potential at which the hydrogen is liberated, the excess potential, the current density, and the catalytic action of the metal may be varied; but since nothing is known in regard to catalyzers for this reaction it was decided to work by choosing the first two factors properly and neglecting the last.

That arsenious oxide could be more readily reduced to arsine in the Marsh generator if the salt of a metal other than zinc was added, was suggested in 1893 by Thiele.[2] In trying to determine large amounts of arsenic he found that he could not get a complete reduction of the arsenic unless stannous chloride was added toward the close. Preliminary experiments made upon the basis of these suggestions showed that arsenic can be quantitatively separated from iron or *other injurious metals* by the addition to the solution of salts of bismuth, tin, lead, and cadmium.[3]

In these experiments dilute sulphuric acid was used, of the concentrations advised by Chittenden and Donaldson, though in some instances hydrochloric acid was added to hasten the solution of the zinc. When salts of lead were added to the generator, hydrochloric acid was always used, since in this case sulphuric acid acts slowly upon the zinc. Forty grams of zinc were used for each determination, and enough of the stannous chloride or other salt added to make the zinc active. The arsenical solution, together with the iron and more of the stannous chloride, was then added drop by drop. By the continuous addition of more acid and stannous chloride the action was kept as rapid as was possible without the loss of arsenic from the heated glass tube, until the zinc was almost all dissolved. In this way it was found that weighable quantities of arsenic could be separated quantitatively from as much as 0.300 gram of iron. It is probable that the separation can be made also from a larger amount, but this was not investigated. It should be remembered that, according to the work of Parsons and Stewart, as little as 0.060 gram of iron is sufficient to prevent the reduction of thirty-one per cent. of the arsenic present.

---

[1] Thus eliminating any possible reduction by the zinc.

[2] *Chem. News*, 67, 125 (1893).

[3] Chapman and Low, *Analyst*, Jan., 1906.

TABLE IV.—EFFECT OF STANNOUS CHLORIDE AND OTHER SALTS UPON THE RETENTION OF ARSENIC.

No. of exp.	Weight of iron or other element.	Weight of $SnCl_2$ or other salt.	Arsenic taken. Milligrams	Arsenic found. Milligrams.
1	0.3126 g. Fe	2.0 g. $SnCl_2$	0.75	0.75
2	0.3126	2.0	0.75	0.74
3	0.3126	1.5	0.75	0.75
4	0.3126	1.5	0.75	0.73
5	0.1160	2.0	0.75	0.74
6	0.0600	2.0	0.75	0.73
7	0.3200	4.0	1.86	1.81
8	0.2250	2.0	1.86	1.85
9	0.1550	2.0	1.86	1.84
10	0.1550	2.5	0.93	0.93
11	0.1550	2.5	4.65	4.58
12	0.1550	3.0	0.93	0.91
13	0.1550	2.0	0.93	0.90
14	0.155	4.0	4.65	4.70
15	0.155	No salt	4.65	(3.38)
16	0.155	No salt	93.60	(72.40)
17	0.155	5.0 g. $SnCl_2$	93.60	91.40
18[1]	0.170	5.0	112.40	113.50
19[1]	0.170	5.00	112.40	112.80
20	0.080	3.0 g. $BiCl_3$	0.93	0.92
21	0.155	3.0 "	0.93	0.93
22	0.155	3.0 "	1.86	1.85
23	0.155	1.0 g. $CdSO_4$	0.93	0.95
24	0.155	4.0 g. $CdCl_2$	4.65	4.55
25	0.155	4.0 "	4.65	4.48
26	1.0 g. $PtCl_4 4H_2O$	No salt	2.79	(2.36)
27	1.0 "	2.0 g. $SnCl_2$	2.79	2.77
28	0.300 g. Fe	2.0 g. $Pb(C_2H_3O_2)_2$	0.93	1.90
29	0.300 "	2.0 "	1.86	1.82
30	0.155 "	No salt	1.86	(0.99)

Numbers inclosed in parentheses ( ) show the retentive effect of salts of iron or platinum, when the salt of another metal is not added.

[1] In experiment 17 the amount of arsenic recovered was slightly lower than it should have been. Since but 40 grams of zinc were used, in experiments 18 and 19 this amount was increased to 100 grams, and the size of the flask to one liter. Under these conditions no difficulty was experienced in the determination of more than a tenth of a gram of metallic arsenic, so this method could be used for the separation of arsenic from iron in ores containing arsenic.

It was found possible to make this separation with either arsenious or arsenic acid when the iron was added either in the ferrous or the ferric state, but the results given above were obtained in experiments where arsenious oxide alone was used.

In the preliminary experiments cadmium salts did not give such good results as when salts of tin were added. This seems due, in part, to the fact that the evolution of hydrogen was much less rapid in the former case. Bismuth salts are less easily purified, and lead salts produce an insoluble sulphate when sulphuric acid is used. For these reasons, most of the experiments were made with stannous chloride. The salts used were purified from arsenic, and all of the other reagents were also purified in cases where arsenic was present.

Good results were obtained by the electrolytic method in the absence of iron when as much as two milligrams of arsenic were present, but the addition of stannous chloride has not produced the same favorable result in the presence of iron as is obtained when the ordinary Marsh generator is used. When zinc electrodes are used in the presence of stannous salts the electrodes dissolve rapidly, so that the conditions are almost the same as those in the ordinary Marsh test.

It was considered possible that a part of the great retentive action of iron salts might be due to a chemical action between the iron salts and the arsine. To test this, the arsine produced in experiments such as those given in Table IV was passed through concentrated solutions of iron salts, with the result that no arsine was absorbed. This, of course, does not prove that compounds are not formed at the surface of the zinc in the generator.

In order to see if there is a connection between the excess potential of the metals and the reducing action of the hydrogen liberated from these metals in the Marsh generator, it was essential to determine a number of excess potentials previously undetermined. These determinations are now in progress, and nearly all of the common and rare metals which can be obtained in a suitable form have been procured for use in this work. The greatest difficulty experienced has been that of keeping the surface of the metals in a proper condition, and at the same time to eliminate the last traces of oxygen from the apparatus.[1]

Approximate determinations of the excess potential were first made by the method of Caspari. The results of these determinations, although made by a method which is only approximate in its results, are of some value in connection with the data presented. It is hoped that more accurate numbers can be presented in the second paper. It is universally recognized that the value of the excess potential of a metal depends to such an extent upon its surface condition and its previous condition as an electrode that it is impossible to obtain concordant values.

---

[1] See Lewis and Jackson, *Z. physik. Chem.*, 56, 199 (1906).

TABLE V.—THE EXCESS POTENTIAL OF THE METALS IN VOLTS AS DETERMINED BY THE APPROXIMATE METHOD OF CASPARI.

Metal.	Excess potential in volts Caspari.	New determination	Tafel[1]
Mercury	0.78	0.74	1.30
Zinc	0.70	0.71	. . .
Lead polished	0.64	0.62	1.30
Lead rough	. .	. .	1.23
Tin	0.53	0.55	1.15
Cadmium	0.48	. . .	1.22
Arsenic		0.39	. .
Bismuth		0.38	1.00
Copper	0.23	0.25	0.79
Cobalt	.	0.22	. .
Nickel	0.21	0.15	0.74
Silver	0.15	0.13	0.93?
Gold	0.02	. . .	0.95
Iron	0.07	. . .	. . . .
Platinum	0.09	0.07	. . . .
Platinum black	0.005	0.002	0.07
Palladium	0.48	0.02	. .
Palladium black	. .	0.002	. .

Temperature = 20° C.

A study was made of the variation of the excess potentials of bismuth and copper with the current density. The curves of excess potential follow in general the equation

$$E = A + B \log I,$$

in which A and B are constants. From the measurements of Caspari and of Tafel[2] it would seem that the values of B for silver and gold are greater than for nickel and platinum. This shows that it is unsafe to draw too definite conclusions as to the relationship between excess potential and the reducing action of hydrogen in the Marsh generator, until the curves of the variation of excess potential with the current density are more definitely determined. That other factors than current density influence the excess potential is shown by the results of Tafel upon the potential of a silver electrode. When the silver cathode was separated from the anode by a porous cell, the potential value for 0.125 ampere per sq. cm. and 2 N sulphuric acid was about 1.5 volts, while, when there was no separating wall between the anode and the cathode, the potential soon fell to 1.15 volts.

---

[1] *Z. physik. Chem.*, 50, 712 (1904). The values given are for a current density of 0.1 ampere per square centimeter.

[2] *Z. physik. Chem.*, 50, 712 (1905).

It will be seen by referring to the values for the excess potential of the metals given in Table V, that those metals which were found favorable to the reduction of the oxides of arsenic to arsine are metals of high excess potential, while those which proved unfavorable were metals of low excess potential.

The one seeming exception to this rule, in the case where a salt of mercury was added, was due to the effect of the mercury in decreasing the speed of the solution of the zinc, just as would be expected when the zinc becomes coated with an amalgam whose excess potential is as great or greater than that of the zinc itself.

That the rapidity of the reduction and its completeness depended also upon the speed with which the hydrogen was evolved, and therefore upon the current density, was proved by varying the speed of solution of the zinc and weighing the arsenic deposited for a certain time interval.

The system used was so complicated that the experiments gave little light as to the catalytic effect of the different metals upon the reduction. That the electrolytic method is more favorable for the investigation of this problem is obvious. It is probable that the reduction of arsenious oxide to arsine takes place in two or more stages, and it is possible that an intermediate reduction product other than arsenic may be found.

When the iron was alloyed with the zinc used in the generator, it had the same injurious effect as if it were added to the solution as a salt,[1] and the addition of stannous chloride proved favorable as before.

If we consider the system previously discussed, that of platinum deposited upon zinc, it is to be expected that, on account of the lower excess potential of the platinum, the hydrogen given off will have a low reducing power. That the amount of arsenic reduced to arsine is less than that added to the generator was proved by a number of experiments, only one of which is listed in Table IV (Experiment 26). If a salt of tin is now added, the tin precipitates upon the platinum (and upon the zinc as well) and covers it in such a way that a new surface is substituted. If this new surface has the same excess potential as tin, the reduction should become more rapid than before. That this is the case has been proved in a number of instances.

When a salt of iron is dissolved in the solution the case is more complex, since practically all of the iron remains in solution, together with a part of the arsenic. Whatever may be the cause of the tendency of iron to prevent the reduction, it is probable that the beneficial action of the tin added is due to an increase of potential at the surface from which hydrogen is liberated.

The separation of arsenic from iron is extremely important in work where only traces of arsenic are present, for almost all substances which contain arsenic also contain small amounts of iron, and in no case is the zinc used free from iron. For this reason, whenever the Marsh method is used, the conditions should be such as are favorable to the separation of the arsenic from the iron which is always present.

---

[1] Parsons and Stewart, *Loc. cit.*

The results of this work should not be understood to mean that the excess potential alone is the determining factor in the reduction, but only that it is one factor. A study of the electrolytic reduction of arsenic and arsenious acids will undoubtedly prove that certain metals of lower excess potential are more efficient cathodes for purposes of reduction than certain other metals of higher excess potential.

It is interesting to note that arsenic itself is a metal of moderately high excess potential, so that, if any arsenic were precipitated upon the zinc, the reducing action of the system would not be materially lessened. The addition of a solution of arsenic to the Marsh generator makes the zinc "active" without the addition of the salt of any other metal.

The fact that the value of the excess potential of the metal added to the generator has an influence upon the reduction, proves that at least one step in the reduction takes place at the surface of this metal, and that at least this part of the reduction is due, therefore, to the hydrogen and not to the zinc.

Summary.

1. The addition of salts of tin, cadmium, lead, or bismuth to the liquid in the Marsh generator makes the zinc "active" without the decrease in reducing power which comes from the platinum or iron commonly added as salts, or as alloys with the zinc.

2. Arsenic may be separated quantitatively from iron and determined in one process by either heating the generator or by adding a salt of one of the metals named above.

3. So far as has been investigated, metals of low excess potential hinder the reduction in the Marsh generator, while metals of high excess potential do not have any injurious action. However, it is not claimed that this will be a perfectly general relation, since the variation of other factors will undoubtedly be great enough to cause exceptions to the general rule.

4. The speed of the reduction of an oxide of arsenic increases with the rapidity of evolution of hydrogen, provided that the latter effect is not due to the addition of a metal of low excess potential; or the speed of reduction depends upon the current density. This is to be expected, since the current density is one factor in determining the electrode potential.

5. The determination of arsenic is made more accurate by the use of a special form of furnace for heating the glass tubes in which the arsenic is decomposed.

6. Since as much as 0.1 gram of metallic arsenic may be separated

from iron and determined quantitatively, this method is applicable to the analysis of ores and other substances containing large amounts of arsenic.

7. The method may also be used for amounts of arsenic as small as 0.001 milligram, but the apparatus must be made much smaller than that described.

STANFORD UNIVERSITY AND THE UNIVERSITY OF MONTANA.

[CONTRIBUTIONS FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF INORGANIC CHEMISTRY.]

ELECTROLYTIC DETERMINATION OF ZINC.

BY ELLWOOD B SPEAR, EDWARD E WELLS AND BRAINERD DYER.

Received February 14, 1910.

Many methods have been proposed for the electroanalysis of zinc,[1] but unfortunately other experimenters have not always been able to get the degree of accuracy that the advocates of a particular method claim it is capable of giving. One of us, while doing some electrolytic determinations of zinc, invariably got high results by several methods. About the same time a paper appeared by Price[2] in which he stated that the values obtained by all electrolytic methods for zinc are too high. The object of this and the succeeding article was to determine, if possible, the magnitude and cause of the error.

The following methods were investigated:

1. The sodium acetate method.
2. The potassium oxalate method.
3. The sodium, or potassium hydroxide method.

The endeavor was made to follow the directions given in the literature as closely as possible while testing each method. Unfortunately, the instructions are sometimes incomplete, especially with regard to the factors, current density, current in amperes and area of cathode surface. It is not sufficient to give the current density, or the current in amperes alone. Two of these factors should be given from which the third can be calculated.

Over 200 determinations with the above methods have been made and it has been found that when the zinc was completely precipitated the results were invariably too high.

The effect of varying the following factors was also investigated:

1. Nature and concentration of the electrolyte.
2. Form and material of the cathode.
3. Current density.

---

[1] "Electro-analysis," E. F. Smith. Elektroanalytische Schnellmethoden, Fischer, "Die Chemische Analyse," Band 4–5.

[2] *Chem. News*, 94, 18 (1906), and 97, 89 (1908).

4. Temperature.

The following tables contain a few results that are typical of those obtained during this investigation:

Preparation of the Solution.—The zinc solutions were made by dissolving a weighed amount of pure zinc (0.2–0.4 gram) in 4 cc. of nitric acid (1.2) and evaporating almost to dryness, after the addition of about 2 cc. of concentrated sulphuric acid. The zinc sulphate was dissolved in water, the electrolyte in question added and the solution made up to the necessary volume. At the completion of the electrolysis zinc was always tested for in the remaining liquid by the methods given in the last part of this article.

In the following tables under "Kind of electrode" A is a rotating (500 revolutions to the min.) copper gauze. B is a platinum dish plated with copper. C is a platinum crucible on which the zinc was directly precipitated. D was a stationary platinum plate covered with a light deposit of copper. E was a stationary, silver gauze.

SODIUM ACETATE METHOD.

No.	Vol. of soln	NaOAc in g.	HOAc drops. 30 per cent.	N. D. Amps.	Time in mins.	Kind of electrode.	Zinc taken.	Zinc obtained	Error Per cent.	Remarks.
33	60	3	6	3.5	25	A	0.2229	0.2250	+0.9	Temp. 40–60°
34	60	3	6	3.5	25	A	0.2229	0.2250	+0.9	"
37	60	8	15	2.5	20	A	0.2229	0.2245	0.7	"
38	80	3	15	5–6	30	B	0.2548	0.2552	0.2	Some Zn lost
39	60	3	6	3	30	A	0.2676	0.2690	0.5	T. 25
40	60	3	6	3	30	A	0.2676	0.2706	1.1	"
43	60	1	..	2	30	A	0.2278	0.2290	0.5	2 g. Na_2SO_4 added
44	60	1	..	2	30	A	0.2440	0.2462	0.9	"
45	60	1	10	2	30	A	0.2482	0.2492	0.4	"
51	60	1	..	5–6	30	C	0.1645	0.1673	1.7	"
52	60	1	..	5–6	30	C	0.1780	0.1810	1.7	"
53	60	1	..	5–6	35	C	0.2080	0.2096	0.7	"

POTASSIUM OXALATE METHOD.

No.	Vol. of soln	$K_2C_2O_4$ in g.	N.D. Amps.	Time in mins.	Kind of electrode	Zinc taken.	Zinc obtained.	Error. Per cent.	Remarks.
19	60	4	4	30	A	0.2393	0.2452	+2.5	Temp. 40–50°
20	60	4	4	30	A	0.2596	0.2632	1.4	"
21	110	4	3–5	35	A	0.2575	0.2608	1.3	Temp. 20°
22	110	4	3–5	35	A	0.2663	0.2705	1.6	"
29	60	10	5–6	60	A	0.2229	0.2242	0.6	60° cooled toward end
30	60	10	5–6	30	A	0.2229	0.2241	0.6	"

POTASSIUM HYDROXIDE METHOD.

No.	Vol.	KOH in g.	N.D.	Time in mins.	Kind of electrode.	Zinc taken.	Zinc found.	Error. Per cent.	Remarks.
3	125	5	5	30	A	0.3344	0.3397	+1.5	
4	125	5	5	30	A	0.3042	0.3120	2.5	
8	125	3	3.3	30	A	0.3164	0.3171	0.2	
10	125	3	3.3	30	A	0.3352	0.3363	0.3	Cooled towards end
11	125	7	0.6	180	D	0.3042	0.3170	4.0	
12	125	7	0.5	180	D	0.3939	0.4040	2.5	
13	125	0.3	0.5–5	25	A	0.2545	0.2569	1.1	KOH added a few drops at a time
14	125	0.3	0.5–5	25	A	0.2495	0.2519	0.9	
15	125	4	3.5	30	E	0.3464	0.3483	0.5	Cooled towards end
16	125	4	3.5	30	E	0.3487	0.3503	0.4	"

When the deposits are good the error is very much smaller than when they are loose- and coarse-grained. One of these bad deposits was obtained and analyzed in the following manner: C. P. zinc was made the anode and a platinum plate the cathode in a sodium hydroxide solution. The current was made high enough to cause the zinc to tree on the cathode and fall off. As fast as this occurred the zinc was removed, washed with water and dried at 150°. About 3 grams were prepared in this manner. On further heating at 150° for 4 hours only a very slight increase in weight (0.6 mg.) took place. Two samples of 1 gram each were analyzed by the ammonium phosphate method and one by the carbonate[2] method. The per cent. of zinc obtained was 88.38, 88.13, 88.17, respectively. The causes for this error are discussed in the following article.

The Detection of Small Quantities of Zinc.—In order to determine when all the zinc is deposited it is necessary to have a convenient and accurate test. The delicacy of the tests for zinc is greatly reduced by the presence of large amounts of the salts of organic acids,[1] *e. g.*, oxalates, where complex zinc salts may be formed, and doubtless many investigators have been misled because of the failure to take cognizance of this fact. Some of these tests have been investigated as follows:

A dilute solution of zinc sulphate (1 cc. contained 1 mg. Zn) was made by dissolving pure zinc in nitric acid, adding sulphuric acid and evaporating just to dryness. Solutions similar to those used in the electrolysis in contents and volume were then made and the delicacy determined by finding the least quantity of zinc that would give a precipitate with the reagent in question. The results are summed up in the following paragraphs in which the concentrations of zinc are given in milligrams per liter.

---

[1] Talbot, "Quantitative Chemical Analysis," page 64. Dakin, *Z. anal. Chem.*, 39, 273 (1900).

[2] Treadwell and Hall, "Analytical Chemistry," Vol. 2, page 117 (1904).

Freshly prepared ammonium sulphide is not a good testing reagent for zinc at room temperatures. Ten mg. sometimes produces no turbidity. The delicacy is improved somewhat by raising the temperature to 50–60°. The objection to polysulphide is the precipitation of sulphur.

Hydrogen sulphide is a very satisfactory reagent. In a neutral solution of zinc sulphate 1 mg. of zinc may be detected at 50–70°. The limit at the same temperature is about 4 mg. if 100 cc. 0.90 ammonia are added. At 10°, with 40 cc. of 0.90 ammonia present, 10 mg. of zinc will not produce any turbidity for several minutes. Hydrogen sulphide, with or without ammonia, is not a delicate test for zinc when large amounts of potassium oxalate are present.

Potassium ferrocyanide is very satisfactory at a temperature between 50 and 70°. The solution should be made acid with 10–15 cc. of sulphuric acid (1.84) and potassium ferrocyanide added until the concentration is about 25 grams per liter. Under these conditions 0.5 mg. of zinc will produce a turbidity even in the presence of large amounts of the salts of organic acids.

[CONTRIBUTION FROM THE MASS. INSTITUTE OF TECHNOLOGY, LABORATORY OF INORGANIC CHEMISTRY.]

ON THE CAUSES OF THE HIGH RESULTS IN THE ELECTROLYTIC DETERMINATION OF ZINC.

BY ELLWOOD B. SPEAR.

Received February 14, 1910.

It has been shown in the previous article that the electrolytic determination of zinc by several methods is attended by high results. The cause must then be due to the presence of some foreign substance in the deposit such as:

1. Enclosure of liquid.
2. Salt precipitated with the zinc.
3. Hydrogen adsorbed or deposited as hydride.
4. Metal deposited with the zinc.
5. Zinc oxide or hydroxide deposited with the zinc.

The first part of this article consists of a detailed consideration of the above-named possibilities and the conclusion is finally reached that the formation of zinc oxide, or hydroxide, is the real cause of the high results. The second part deals with theoretical considerations.

The method of preparation of the solutions to be electrolyzed and the experimental conditions during the electrolysis were, except where otherwise stated, the same as in the preceding article.

Enclosure of Liquid.—It is extremely improbable that a smooth deposit of zinc would enclose a liquid, yet the best deposits are too high. Heating the dried deposit to 200° should reduce the weight, if any liquid were present. This was done repeatedly with different deposits and an insignificant increase in weight was always noticed, due, doubtless, to a very slow oxidation of the zinc. Further, electrolytic zinc that had been deposited from a solution that contained only sodium and zinc sulphates was carefully washed with water, alcohol and ether successively, dried and weighed. This weight was found to be invariably too high, if all the zinc had been deposited from solution. These deposits were next dissolved in hydrochloric acid, evaporated almost to dryness and the residue dissolved in a few cc. of water. On adding barium chloride not a sign of turbidity resulted on long standing. If any of the liquid had been enclosed some turbidity must have been in evidence under the conditions of the experiment. The last argument would also apply if any salt had been precipitated with the zinc.

Hydrogen Adsorbed or Deposited with the Zinc.—That any appreciable quantity of hydrogen is not contained in the deposits was proven in the following manner: About 0.4 gram of zinc was deposited on a copper gauze electrode from a sodium acetate solution. The deposit was in every case from 0.7 to 2.0 per cent. too high, which would correspond to 3 to 8 mg., or 40 to 100 cc. of hydrogen gas. The gauze electrode with the zinc deposit was put into the ignition tube *A* (Fig. 1) and covered with mercury. Flask *B* was filled to the neck with water and connected with the water in *C* by a short tube. *B* served as a trap to catch any mercury that might distil over. *C* was a 100 cc. graduated tube and was connected with the water in *D*. The mercury was boiled in *A* for 20 minutes. When the apparatus had cooled the water rose in *C* to the same level at which it stood before the heating. If any hydrogen had been contained in the zinc deposit it would have been given off and caught in *C* when the zinc formed an amalgam with the mercury.

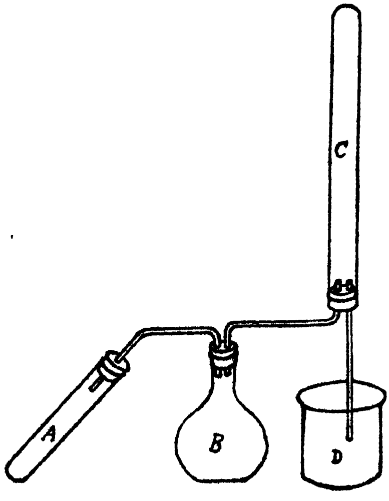


Fig. (1).

Metal Deposited with the Zinc.—If the high results were caused by the presence of a foreign metal, such as sodium, in the deposit, then there should be some relation between the magnitude of the error and the concentration of the sodium salts present during the electrolysis. This proved not to be the case, although the concentration was varied from zero to 200 grams per liter. Furthermore, two of these deposits were analyzed for sodium as follows: About one-half gram of the deposit was dissolved in hydrochloric acid and the zinc precipitated with ammonium carbonate. After acidifying with hydrochloric acid the filtrate was evaporated to dryness and the ammonium salts expelled. On once more precipitating the remaining zinc in a small volume with ammonium carbonate and expelling the ammonium salts the residue was not weighable. 10 to 20 mg. of sodium chloride must have remained if the high results are to be accounted for by the presence of sodium in the deposits.

Zinc Oxide or Hydroxide Deposited with the Zinc.—An attempt was made to reduce the zinc oxide by heating the deposit in a current of hydrogen gas. Owing to the volatility of the zinc and also of the zinc oxide, this was found to be impracticable. Reasons for believing in the presence of the oxide, or hydroxide, in the deposit are given below:

Zinc deposits from sulphuric acid solutions, where impoverishment of zinc in the cathode portion is prevented, have highly reflecting metallic surfaces and are found to be pure zinc by the best gravimetric methods. This was proven in the following manner: One gram of zinc sulphate was dissolved in 50 cc. of water to which was added 1 cc. of sulphuric acid (1.20). A rotating platinum crucible was made the cathode, pure zinc the anode, and the zinc deposited with a current of one ampere. The deposit was washed with water, alcohol, and ether, respectively, dried and weighed. The zinc was then dissolved in a few cc. of hydrochloric acid and the crucible again weighed. The zinc was determined by the phosphate method.[1] The results were as follows:

Elec.	Zn taken.	Zn found
1	0.1890	0.1891
2	0.1837	0 1841
3	1.1054	1.1040

Zinc deposits from neutral or dilute alkaline solutions have little or no metallic appearance. Those from acetate or oxalate solutions are dull gray. The upper portion of the deposit is often quite white, resembling zinc hydroxide. Deposits from strongly alkaline solutions are gray to black, depending upon the fineness of division of the metal; they are never smooth or metallic if the cathode portion becomes impoverished with regard to zinc. These finely divided, black deposits decompose water so rapidly, if sodium salts are present, that the bubbles of hydrogen gas can be seen rising from the surface of the metal. If they are wet with water and let dry in a desiccator they increase in weight and become quite white.

---

[1] Talbot, "Quantitative Analysis," p. 64. Dakin, *Ztschr. anal. Chem.*, 39, 273 (1900).

Pure zinc deposits obtained from sulphuric acid solutions increase in weight and become white and non-metallic on the outside if made cathode for some time in a nearly neutral or slightly alkaline solution. In very dilute sulphuric acid solution (10 cc. (1.20) per liter) the appearance and weight do not change. In strongly acid or alkaline solutions the zinc dissolves faster than it is reprecipitated by the current, and the weight of the electrode consequently decreases. This is shown by the following experiments:

Pure zinc deposits were obtained from sulphuric acid solution according to the method already given. They were then dried, weighed, made cathode in a neutral sodium acetate solution free from zinc and electrolyzed for 30 minutes with a current density of 2.5 amperes. The results are given below. Column 1 is the weight of the zinc obtained by the deposition from dilute sulphuric acid solution; column 2 gives the weight after 30 minutes:

1.	2.	
0.1833	0.1839	Deposits became non-metallic in appearance.
0.5202	0.5237	" " " "
0.2499	0.2508	" " " "
0.2787	0.2787	Very dilute acid. No change in appearance.
0.1810	0.1783	Acid stronger. No change in appearance

In order to prove that the oxidation of the zinc did not take place after the electrolysis while the electrode was being washed and dried, the following experiments were carried out: 0.2 to 0.4 gram of zinc was deposited from a sodium acetate solution according to the best methods that we have found. Copper gauze was employed as cathode and the deposits were all excellent. When the electrolysis was finished, without disconnecting the current or stopping the electrode, the solution was gradually replaced by water, alcohol and ether, respectively, and finally with ether that had been dried with sodium. The electrode, completely submerged in ether, was now put into a covered dish and the ether evaporated off in a current of hydrogen. In this way the deposit was never allowed to come in contact with the air until the zinc was quite dry. It would, therefore, be impossible for the oxidation of the zinc to take place after the electrolysis. The results of several analyses carried out in this manner are given below. Column 1 gives the weight of pure zinc taken and column 2 the weight of the deposit:

1.	2.
0.2106	0.2129
0.2439	0.2472
0.2513	0.2592
0.2671	0.2855
0.2843	0.2894
0.2713	0.2747
0.3014	0.3033
0.3177	0.3238

When solutions of sodium acetate are electrolyzed they become alkaline, owing to the formation of sodium hydroxide at the cathode and the oxidation of the acetate to carbon dioxide and subsequent escape of this gas at the anode. If the solution is not sufficiently concentrated with respect to sodium acetate the zinc will be precipitated out as hydroxide as soon as the solution becomes alkaline. If too much free acid is present all the zinc cannot be precipitated. If an excess of the acid is avoided, then the layer of liquid in the immediate neighborhood of the cathode becomes slightly alkaline, zinc hydroxide is formed in this layer and is precipitated with the zinc, possibly because it is enclosed or adsorbed.

The most obvious remedy that suggests itself would be to make the solution so strongly alkaline that the formation of zinc hydroxide would be impossible. This has been found to be impracticable because hydrogen is evolved so rapidly at the cathode that the character of the deposit is destroyed as soon as the solution becomes depleted with respect to zinc. Furthermore, strong alkaline solutions attack zinc deposits, especially those that are finely divided, so vigorously that it is almost impossible to completely precipitate the zinc. If the current density is increased, the solution foams because of the rapid evolution of hydrogen and a bad deposit results.

Theoretical Considerations.—A certain potential exists between a pure zinc electrode and a solution of zinc salts of given concentration. This potential depends upon the concentration of zinc ions, not upon the total amount of zinc in the solution and increases as the concentration of the zinc ions decreases. Therefore the applied electromotive force necessary to deposit zinc from a solution of its salts must be increased as the electrolysis proceeds. These facts are expressed mathematically by the following well-known equation:

$$\pi_{Zn \rightarrow soln} = E_{Zn} - (RT/2F)\ ln\ C_{Zn^{++}} \qquad (1)$$

π is the fall of potential in volts between the electrode and the solution, E_{Zn} is a constant equal to π when the concentration of the zinc ions is unity, R is the gas constant, F one Faraday's equivalent, C the concentration of the zinc ions in gram mols. per liter.

A similar equation must apply to hydrogen at atmospheric pressure surrounding a reversible electrode and a solution containing hydrogen ions:

$$\pi_{H_2 \rightarrow soln} = E_{H_2} - (RT/2F)\ ln\ C^2_{H^+}. \qquad (2)$$

If the hydrogen electrode is taken as zero, the potential between pure zinc and a normal solution of its ions is 0.77 volt.[1] The limiting concentration at which zinc can be quantitatively determined is about 10^{-5}. Assuming complete dissociation and putting these values in equation

---

[1] Wilsmore, *Z. physik. Chem.*, 35, 308.

(1) we get as a result 0.91 volt. The potential of the hydrogen electrode aginst a neutral solution calculated by equation (2) is 0.41 volt. It would, therefore, be impossible to precipitate zinc electrolytically from a neutral solution were it not that the overvoltage of hydrogen on zinc electrodes is high. For actual working conditions, then, we must add to equation (2) another term, η, which is a variable and is dependent upon the nature of the electrode and upon the current density.

By decreasing the concentration of the hydrogen ion *i. e.*, by making the solution alkaline, it would be more and more difficult to evolve hydrogen at the electrode. Unfortunately, however, the concentration of the zinc ion is diminished to a far greater extent than that of the hydrogen ion by the addition of a base, and thus the conditions are still more unfavorable for the complete precipitation of the zinc. This is apparent from the following considerations:

The equilibrium equation for the dissociation of water is

$$(H)(OH) = K_1 \text{ or } (H)^2 = K_1^2/(OH)^2. \qquad (3)$$

Zinc hydroxide is an amphoteric electrolyte and therefore dissociates both as an acid and as a base. For the dissociation as an acid we have the equation

$$(H^+)^2(ZnO_2^{--})/(Zn(OH)_2) = K_2. \qquad (4)$$

As a base,

$$(Zn^{++})(OH_2^-)^2/(Zn(OH)_2) = K_3. \qquad (5)$$

Substituting (3) in (4) we get

$$K_1^2(ZnO_2^{--})/(OH)^2(Zn(OH^-)_2) = K_2. \qquad (6)$$

Dividing (5) by (6) and transposing we get

$$(Zn^{++})(OH^-)^4/(ZnO_2) = K_3K_1^2/K_2 = K_4.$$

We see, then, that while the concentration of the hydrogen ion is inversely proportional to the concentration of the hydroxyl ion raised to the first power, that of the zinc ion is inversely proportional to the concentration of the hydroxyl ion raised to the 4th power. From these considerations, in connection with equations (1) and (2), it will be easily seen that it becomes relatively more and more difficult to precipitate zinc as we increase the concentration of the hydroxyl ion.

Summary.

In this article it has been experimentally shown that the high results obtained in the electrolytic determination of zinc are not caused by the enclosure of liquid, presence of a salt, hydrogen in the deposit, nor by the presence of another metal. The true cause is the deposition of zinc oxide or hydroxide with the zinc.

Theoretical considerations for the electrodeposition of zinc have been discussed and reasons for the rapid evolution of hydrogen in strong alkaline solutions have been given.

NOTES.

Titration of Ferrous Salts in the Presence of Hydrochloric and Phosphoric Acids.—Referring to a recent article by Elwyn Waller concerning the use of calcium phosphate in solutions containing hydrofluoric acid, when the solution is to be titrated by potassium permanganate, to obviate the bad effect of the hydrofluoric acid on the permanganate, it seems to me that the beneficial agent in this reaction is really the phosphoric acid.

I wish to state that the use of phosphoric acid alone in iron solutions to be titrated by potassium permanganate was first proposed by me about two years ago; my experiments and conclusions were published in the *Western Chemist and Metallurgist*, for Nov., 1907.

In trying to devise an improved method for the determination of iron in bone-black (which is nearly pure calcium phosphate), I found that the solution acidulated with hydrochloric acid could be titrated directly by permanganate, with great accuracy, the results checking with those made by the standard bichromate method, to hundredths of a per cent.

As the hydrochloric acid present seemed to have no effect on the permanganate, I reasoned that this must be due to the action of the phosphoric acid.

The method as applied to bone-black was as follows: The hydrochloric acid solution of the bone-black, after filtering off the carbon, was nearly neutralized by sodium carbonate to faint opalescence, then acidulated with 1 or 2 cc of concentrated hydrochloric acid, the carbon dioxide expelled, the solution reduced by addition of sodium sulphite, the sulphur dioxide expelled, the solution diluted with cold water to about 300 cc., and titrated with potassium permanganate.

After securing such favorable results on bone-black, I was impelled to try the method in the titration of iron in iron ores. I found it worked perfectly and gave extremely accurate results, provided one or two precautions were observed, namely, the use of a minimum amount of hydrochloric acid, not over five to ten cubic centimeters of concentrated acid, at the most, titration in a cold solution of about 300 cc. volume, and the avoidance of stannous chloride in reducing the iron.

The iron may be advantageously reduced by sodium sulphite, by aluminium, by zinc, or by test-lead. If test-lead be used, the reduction may be satisfactorily accomplished in a strongly acid solution, or in one that has been almost neutralized by sodium carbonate; and where we cannot avoid the presence of much hydrochloric acid, this reduction by test-lead in a nearly neutral solution would appear to be the best; or we can use zinc dust (powder), which also acts most rapidly in a nearly neutral solution.

It must not be thought that this improvement is simply a modification of the old Zimmerman-Reinhardt method. In that method, the manganese sulphate takes up hydrochloric acid, becoming manganese chloride, and the phosphoric acid present was supposed simply to decolorize the ferric iron and keep the solution colorless. But we see now that the phosphoric acid really plays a double rôle, and the addition of manganese sulphate and sulphuric acid is not at all necessary.

As the titration of iron solutions by potassium permanganate is much the preferable method in technical work, owing not only to its rapidity and ease of execution, but also to the sharpness of the end reaction, it seems to me that any suggestion that will tend to improve the method and make it more general of application cannot fail to be of great value to technical chemists generally. GEORGE J. HOUGH.

The Action of Coke on Solutions of Ferric Chloride.—In a previous communication[1] the author gave some data showing the extent to which iron is removed from a solution of ferric chloride by filtration through coke.

The opinion was then expressed that this action was largely due to sulphur compounds which had not been wholly removed from the coke.

A new series of experiments has been made to test this view, such precautions to eliminate sulphides from the coke being taken as the author's slender laboratory equipment would permit, and the results have confirmed the author in his opinion. The conclusion is, in brief, that no iron was taken up by coke so treated, from an approximately decinormal solution of ferric chloride under a variety of conditions, though a part of the salt was reduced to the ferrous condition. Coke similarly prepared did not abstract any copper from an approximately decinormal solution of cupric chloride. This last is in accord with the statement of W. O. de Coninck,[2] who, however, originally stated that the iron was abstracted from ferric chloride solution.

The following are the details of the new experiments:

Preparation of Coke.—Ordinary coke was ground and passed through a sieve of 100 meshes to the inch. It was then treated with hydrochloric acid, and after that with a mixture of concentrated hydrochloric and nitric acids. After standing a few days the acids were decanted off and the coke washed repeatedly with water, dried in the air and on the steam bath. Any higher temperature was avoided lest by local superheating residual sulphates should be converted into sulphides. The coke so treated, when heated with hydrochloric acid, gave no fumes capable of darkening lead test-paper.

Ferric Chloride Solution.—To a concentrated and acid solution of ferric chloride, sodium carbonate was added in such quantity that, though still acid to litmus, the color became essentially that characteristic of basic chloride. The solution was then diluted to the desired strength. Titration with standard potassium dichromate showed 1 cc. = 0.0053017 gram iron.

---

[1] THIS JOURNAL, 31, 461.

[2] *Compt. rend.*, 130, 1551.

In each experiment 40 grams of coke and 100 cc. of ferric chloride were used.

Experiment 1.—The solution was percolated, with the help of a filter pump, through the coke contained in a "Jones reductor" tube. The percolated liquid was then passed through a dry filter paper.

Experiment 2.—Coke was placed in a flask and ferric chloride solution was added to it. The flask was stoppered and allowed to stand 24 hours; its contents were then filtered through a dry paper.

Experiment 3.—Similar to Experiment 2, but that the time was 1 hour only.

Experiment 4.—Similar to Experiment 3, but that a portion of the mixture was removed and filtered after standing only 15 minutes, while the remainder was allowed to stand for a whole hour, so that two separate filtrates were obtained.

Each of the filtrates from the foregoing experiments was titrated with potassium dichromate after treatment with stannous and mercuric chloride in succession. It was found that, as before being in contact with the coke, 1 cc. in each case contained 0.0053017 gram iron. Under the conditions of each experiment it was found that a part of this iron had been reduced to the ferrous state, but the amount of this reduction was in no case determined.

Experiment 5.—A solution (as nearly as possible neutral) of cupric chloride was substituted for that of ferric chloride, but the conditions were otherwise as in Exp. 3. The concentration of the cupric chloride solution was such that 1 cc. = 0.006301 g. Cu. It was unaffected by the addition of the coke, as proved by subsequent titration with sodium thiosulphate.

ALFRED TINGLE.

LABORATORY OF THE CHINESE IMPERIAL PEI YANG MINT,
TIENTSIN, CHINA.

Note on the Paper Entitled "Some Organic Tungstates."—In the June number of the JOURNAL I published a brief paper entitled "Some Organic Tungstates." The paper described and identified a number of tungstates of aliphatic amines. I have since received a letter from Dr. Lederer, of the Westinghouse Metallfaden-Gluhlampenfabrik, claiming priority and enclosing a copy of English patent No. 27,002, 1906, in which the following statement occurs:

"For this purpose advantage is taken of the fact that the trioxides and acid hydrates of the said metals (tungsten and molybdenum) combine with ammonia or with mono- and polyamines to form salts, and these salts, either alone or mixed together, with or without the addition of other tungsten or molybdenum compounds or of the metals themselves, are formed into a paste by the addition of an agglutinant, which paste is formed into filaments which are then heated."

From the above it is evident that Dr. Lederer experimented with compounds of tungsten, similar to those described in my paper, with a view to their use in the incandescent lamp industry, but did not isolate the compounds nor determine their composition by analysis. This was the main purpose of my paper. JOHN B. EKELEY.

PARIS, January 10, 1910.

THE BASIC PROPERTIES OF OXYGEN: COMPOUNDS OF DIMETHYLPYRONE AND THE HALOGEN HYDRIDES.

BY D. MCINTOSH.

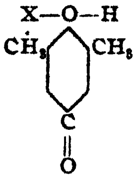
Received February 12, 1910.

In 1899 Collie and Tickle[1] produced crystalline compounds by the addition of various acids to dimethylpyrone. They showed that neither water nor carbonic acid was eliminated by this treatment and that a simple ratio existed between the molecular quantities of the two reacting substances. To explain their results in terms of the current valency theory, they advanced the view suggested many years earlier by Friedel, that in certain compounds oxygen may act as a tetravalent element (the oxonium theory).

Since Collie and Tickle's paper appeared, additive complexes of substances containing oxygen have been widely studied by Baeyer and Villiger, Kehrmann, Hantzsch, Werner and many others.

The salts of dimethylpyrone have naturally undergone careful investigation. Collie and Steele[2] have produced compounds with iodine and hydriodic acid, Weinland and Reischle[3] combinations with hydrofluoric acid, while Plotnikov[4] has described basic and acid salts with chloro- and bromo-acetic acids. The constitutions of these compounds are explained by the assumption of a tetravalent oxygen atom or by the subsidiary bonds according to Werner's theory.

In Collie's first paper dimethylpyrone was represented as a ring containing two divalent oxygen atoms, which for discussion may be termed the ethereal and the carbonyl oxygen atoms. The salts of dimethylpyrone were supposed to have the acid attached to the ethereal oxygen atom, although no reason for its selection was given; and the compounds were represented as



---

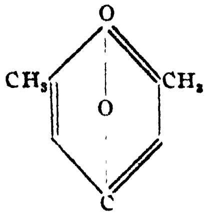
[1] *J. Chem. Soc.*, 75, 710.

[2] *Ibid.*, 77, 1114 (1900).

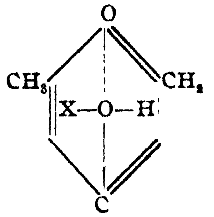
[3] *Ber.*, 41, 3671 (1908).

[4] *Ibid.*, 42, 1154 (1909).

Recently Collie[1] has changed his views regarding the composition of the pyrone and its salts. The former is supposed to have a tetravalent oxygen atom, and in the latter the acid is attached to the carbonyl oxygen atom. The constitutions given are:



and



This hypothesis is strengthened by the work of Homfray[2] and also by the spectroscopic measurements of Baly.[3] On the other hand, Willstäter and Pummerer[4] give reasons why the pyrone itself cannot have a tetravalent oxygen atom and inferentially why its salts cannot have the formulas attributed to them.

In a former paper[5] I attempted to show that some of the compounds regarded by Baeyer and Villiger as containing tetravalent oxygen atoms were merely cases of solid solution, while others formed from hydroferrocyanic acid and the alcohols did not differ in structure from salts with alcohol or water of crystallization. Dimethylpyrone, like ferrocyanic acid, is a solid at ordinary temperatures, and since its salts might be looked on as pyrone with "acid of crystallization," I have examined some of its compounds over a considerable temperature range.

Materials.—The dimethylpyrone was purchased from Merck. No process of purification was thought necessary as its salts of the halogen acids were identical with those described by Collie and Tickle. The halogen hydrides were prepared and liquefied in the ordinary way. The hydrogen fluoride was obtained by distillation of a pure solution of the acid, and experiments with it were carried out in platinum vessels.

Since the formation of compounds is often indicated by electrical conductance in solution, measurements of dimethylpyrone in hydrogen bromide at —78° and in hydrogen chloride at —100° were made. The results are given in the tables and shown in the diagram:

---

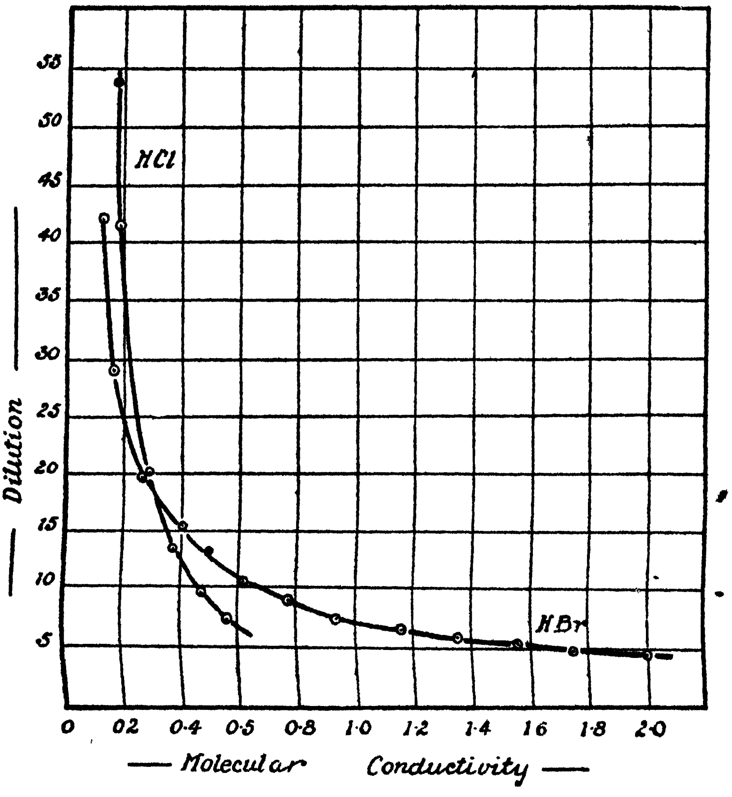
[1] *J. Chem. Soc.*, 85, 973 (1904).

[2] *Ibid.*, 87, 1443 (1905).

[3] *Ibid.*, 96, 144 (1909).

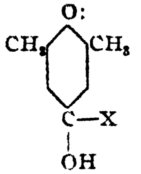
[4] *Ber.*, 37, 3740 (1904); 38, 1461 (1905).

[5] THIS JOURNAL, 30, 1097 (1908).



Hydrochloric acid.		Hydrobromic acid.	
Dilution.	Molecular conductance.	Dilution.	Molecular conductance.
93.0	0.18	42.0	0.13
53.8	0.18	29.2	0.17
41.4	0.19	19.5	0.27
20.0	0.29	15.4	0.41
13.3	0.38	13.3	0.49
9.6	0.48	10.6	0.62
7.4	0.57	9.0	0.78
		7.5	0.94
		6.7	1.16
		5.9	1.36
		5.4	1.56
		4.9	1.75
		4.3	2.05

Dimethylpyrone itself cannot be looked on as an electrolyte. It must unite with the hydrobromic acid, otherwise the conduction of electricity would be impossible. The union cannot take place with a halogen and hydroxyl attached to the carbon, as suggested by Werner, for this compound



should not be ionized. The pyrone moves to the cathode during electrolysis, so the halogen is not attached to the oxygen by a double bond. Further, since the molecular conduction increases with concentration—as it does with all substances containing oxygen and nitrogen in these solvents—complex ions must be formed.[1] We may thus expect compounds in which the pyrone and acid are not present in equimolecular proportions.

Hydrochloric Acid Compounds.—A solution of dimethylpyrone in aqueous hydrochloric acid was kept in a vacuum desiccator till dry. It contained 22.6 per cent. acid and was, therefore, $C_7H_8O_2HCl$. Another specimen, dried between filter papers, gave 19 2 per cent. acid, corresponding to $C_7H_8O_2HCl.2H_2O$. These compounds were first prepared and described by Collie and Tickle.

Dimethylpyrone dissolves readily in liquefied hydrogen chloride with an evolution of heat, noticeable, but small compared with that given by ether, etc. A crystalline substance soon separates out, which melts sharply at —25°. Analyses of different preparations gave 42.6, 45.5, 44.1 and 42 7 per cent. acid. $C_7H_8O_2.2HCl$ contains 36.4, $C_7H_8O_2.3HCl$, 46 9 per cent.

Evidence of the existence of a more complex compound with a much lower melting point was obtained. The difficulty of removing the excess of acid was so great that this body was not examined further.

Hydrobromic Acid Compound.—From an aqueous solution of hydrobromic acid and dimethylpyrone compounds containing from 39.3 to 40 per cent. acid were produced. By dissolving the pyrone in the anhydrous acid and allowing the excess to evaporate salts with 38.9, 39 2, 38.4, 39.3 per cent. acid were made at various times. $C_7H_8O_2HBr$ contains 39.5 per cent. acid (Collie and Tickle). In anhydrous hydrogen bromide dimethylpyrone forms an oily liquid which dissolves easily. At the saturation point a compound probably containing one molecule of acid appears and this floats on the hydrobromic acid and dissolves but slowly. When the saturated solution is allowed to stand or when a crystal of the pyrone is added quickly with a stirrer, prismatic crystals (probably orthorhombic) with faces appear. These crystals give, on analysis:

Sample I,	74.7; 75.1 per cent. acid.
Sample II,	74.2; 75.1 per cent. acid.
Mean,	74.8 per cent. acid.

---

[1] Steele, McIntosh and Archibald, *Z. physik. Chem.*, 52, 129 (1906).

This compound is doubtless $C_7H_8O_2 4HBr$, which contains 72.3 per cent.

When warmed, the tetrahydrobromide melts sharply at —59°, the excess of acid quickly evaporates, and a solid reappears. This substance has a high vapor pressure and when "dried" at —35° contains 59.5, at - 13° 53.2 per cent. acid, which corresponds to $C_7H_8O_2 2HBr$. It melts at —2° and is converted into the compound containing one molecule of acid. Vapor pressure measurements have failed to show the existence of a compound containing three molecules of acid.

Hydriodic Acid Compounds.—Dimethylpyrone dissolves, but less readily, in hydrogen iodide than in the bromide, and at a low temperature crystals separate out. These contain 83.3, 83 6 and 84.6 per cent. acid in three preparations, while $C_7H_8O_2.4HI$ has 82 2 per cent.

At —42°, $C_7H_8O_2.4HI$ melts and a substance with 69 8 per cent. acid separates, which in its turn liquefies at + 7° and yields $C_7H_8O_2HI$. A compound of one molecule pyrone and two of hydrogen iodide contains 67 4 per cent. acid.

Hydrofluoric Acid Compounds—Since fluorine does not unite directly with oxygen, oxonium compounds with hydrofluoric acid should prove of the greatest interest. Landolph[1] claims to have produced two substances in which hydrogen fluoride was united with acetone, and quite recently Weinland and Reischle[2] describe two dimethylpyrone hydrofluorides. The formula $C_7H_8O_2.3HF.0\ 5H_2O$ is given to one prepared from the aqueous acid, the other from an alcoholic solution is represented as $C_7H_8O_2 3\ 5HF0\ 5H_2O$.

Stable compounds of pyrone and hydrofluoric acid are not easy to prepare. In one experiment an aqueous solution of acid and dimethylpyrone was kept over sulphuric acid and potash in a vacuum desiccator. When dry the salt contained 20 3 per cent. acid. After two weeks the acid content had fallen to 15.1 per cent.; two weeks later to 13 1; and after standing two months longer, only 10 7 per cent. acid remained.

A crystalline preparation, made with a large excess of acid, when dried between filter papers, held 37 7 per cent.; after two weeks in a desiccator this was reduced to 30.8 per cent. acid.

A third sample, made by mixing pyrone and acid in approximately molecular proportions, gave, when dried, 14.9 per cent. acid; after two weeks further drying, 13.9 per cent., which corresponds to the formula $C_7H_8O_2HF$. But after five months the acid had fallen to 9.6 per cent. If compounds of dimethylpyrone and hydrofluoric acid are formed they are neither so simple nor so stable as those with the halogen hydrides.

---

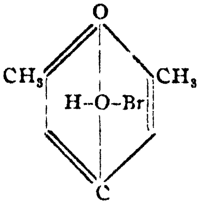
[1] *Compt. rend.*, 86, 1463; 96, 580.

[2] *Loc. cit.*

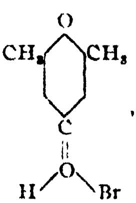
Note.—Anhydrous hydrofluoric acid is unlike the halogen hydrides. When treated with ether, acetone, etc., much less heat is evolved and compounds, if formed, do not crystallize out easily.

We have seen that hydrobromic acid unites with dimethylpyrone to give three stable compounds containing one, two and four molecules of acid. Since hydrobromic acid does not polymerize even when liquefied, any theory to explain the linking of the acid in the simplest compound should apply equally well to the others. We may regard these additive compounds as pyrone with "acid of crystallization," or we may ascribe formulas to them in which oxygen has a higher valency than two.

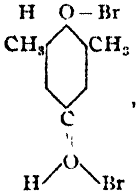
If we accept Collie's representation of the constitution of dimethylpyronehydrobromide,



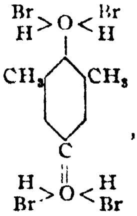
it is difficult to give a satisfactory explanation of the formation of the other salts, unless we admit the possibility of the linking between the two oxygen atoms being broken at such a low temperature. But if we regard the dimethylpyrone itself as a substance with two divalent oxygen atoms we may represent the three salts as



,



,



,

the first containing one, the second two tetravalent, and the third three hexavalent oxygen atoms.

In the most complex salt the oxygen is supposed to function as a hexad, and this may be objected to as unusual and unnecessary. Yet the same arguments advanced for the tetravalency of oxygen apply equally strongly to its hexavalency here; and the position of this element in the sixth column of the periodic table permits the view that its valency may vary as does that of sulphur, selenium and tellurium.

ELEMENTARY ANALYSIS BY MEANS OF A CALORIMETRIC BOMB.

BY HAROLD L. HIGGINS AND ALICE JOHNSON.

Received January 24, 1910.

Since the complete oxidation of organic material, with the quantitative conversion of carbon to carbon dioxide, and of hydrogen to water, presents the greatest difficulty in elementary organic analysis, it is not surprising that particular attention has been paid to making use of the ideal conditions of oxidation obtained inside of a calorimetric bomb. Burning substances in oxygen at a pressure of 25 atmospheres results, usually, in complete oxidation with minor products of combustion, particularly the oxidation of a small amount of nitrogen to nitric acid.

One chief objection to the use of the bomb for ordinary elementary analysis has been the fact that about 1 gram of substance is required,[1] and in many instances, particularly in the field of organic chemistry where frequently but a small amount of material may be available, this precludes the use of the method. On the other hand, in many researches where both the heat of combustion and an elementary analysis are desired, the bomb can be used to great advantage.

In metabolism experiments, either with men or with animals, where it is desired to determine not only the energy ba'ance but likewise the carbon and hydrogen balance, elementary analysis by the bomb is of especial value. Under these conditions, it is necessary to determine both the heat of combustion of the food, feces, and urine, and the amount of carbon and hydrogen in these products; and the simultaneous determinations allow a great saving in time. Usually the substances to be dealt with are in sufficient quantities to permit of large samples, and of duplicate combustions. With coal and other fuels, simultaneous determinations of heat and elementary analyses may also be made where the percentages of carbon and hydrogen present in the coal are desired in addition to the energy value as represented by the heat of combustion.

The Determination of Carbon.—The most common method of determining carbon by the calorimetric bomb has been to collect, in potassium hydroxide or soda lime, all the carbon dioxide formed during the combustion of the substance and to weigh the amount collected. Berthelot,[2] and later Hempel,[3] determined carbon in this way, using a one-valve bomb. The last traces of carbon dioxide were removed by suction, the gas being swept out several times and the bomb refilled with dry air. The method is simplified, however, by using a bomb with two valves, as shown by Kröker[4] and Fries,[5] the bomb being eventually freed of carbon dioxide by passing air through it.

Zuntz and Frentzel[6] in 1897 suggested a method for making carbon determinations with the bomb, wherein they found the total weight or volume of the gases resulting from the combustion and by analyzing these gases, they were able to calculate the total amount of carbon dioxide present. Following this suggestion we have, under the direction of Professor Benedict, developed a method which seems to offer excellent opportunities for routine carbon analyses, which are sufficiently accurate for the most exact physiological experimenting. According to this method, we first weigh the gas at the end of the combustion and then determine the carbon dioxide in a sample by means of a Haldane gas analysis apparatus.[1] Knowing the weight of the gas, the percentage of carbon dioxide, and the amount of nitrogen present, we can calculate the amount of carbon dioxide present by the use of a formula obtained from the following equations:

---

[1] Hempel obviated this objection by the use of a small autoclave similar to the bomb, whereby smaller amounts of substance could be burned more satisfactorily, *Ber.*, 30, 202 (1897). See also Langbein, *Chem.-Ztg.*, 38, 1055 (1909).

[2] Berthelot, *Compt. rend.*, 114, 317 (1892), and 129, 1002 (1899).

[3] Hempel, *Loc. cit.*

[4] Kröker, *Z. Ver. Rubenzücker-Industrie*, 46, Heft 482. *Ber.*, 30, 606 (1897).

[5] Fries, This Journal, 31, 272 (1909).

[6] Zuntz and Frentzel, *Ber.*, 30, 380 (1897).

$$(1) \qquad x + y = c - a.$$

$$(2) \qquad (x/1.43 + y/1.966 + a/1.26)\, b/100 = y/1.966.$$

In these equations, a equals weight of nitrogen gas; b, per cent. carbon dioxide in gas; c, weight of gas; x, weight of oxygen; and y, weight of carbon dioxide. The gas in each instance is that in the bomb at the end of the combustion. Solving for y, we obtain:

$$y = (c + 0.137a)/(0.2727 + 72.73/b) = \text{weight of carbon dioxide},$$

or

$$\text{the weight of carbon}^{2} = 3y/11 = (c + 0.137a)/(1 + 266.67/b)$$

Thus, having the total weight of carbon in the bomb, the percentage of carbon in the substance is readily obtained, after applying corrections for the carbon in the kindler, in the igniting thread, and in the oxygen used.

The Determination of Hydrogen.—Berthelot[3] suggested that the bomb may be used in determining hydrogen by driving out all of the water as vapor and absorbing and weighing it in a dehydrating agent, such as concentrated sulphuric acid or calcium chloride. He immersed the bomb in a water bath and exhausted and admitted air alternately. Kröker,[4] with a two-valve bomb, was able to simplify this process, but the method has the following decided disadvantages: (1) The presence of nitric acid (as well as sulphuric acid, when the substance burned contains sulphur) makes it difficult to expel all of the water and nothing else, and furthermore, these acids tend to attack the valves of the bomb; (2) the heating of the bomb in the bath also increases the liability to injure the enamel lining; (3) it is very difficult to get the interior of the bomb perfectly dry at the beginning of the combustion, as is necessary when this method is used; (4) the operation is very time-consuming.

---

[1] Haldane, *J. Physiol.*, 22, 465 (1897).

[2] 0.137 represents (molecular weight oxygen/molecular weight nitrogen) — 1; 266.67 represents 100 molecular weight oxygen/atomic weight carbon.

[3] Berthelot, *loc. cit.*

[4] Kröker, *loc. cit.*

Langbein[1] determined the water formed by placing a drying glass containing phosphorus pentoxide within the bomb, expelled most of the nitric acid by passing air through the bomb in a bath at 100°, and determined the sulphuric acid by titration. Hempel,[2] using a small autoclave similar to the bomb, drove out only a part of the water, and collected it in a calcium chloride tube. The remainder was weighed in the autoclave itself, the water representing the difference in weight of the autoclave when empty as compared with its weight after the combustion gases had been swept out, corrections being applied for nitric acid, for ash, and for the water formed from the kindler. We have applied Hempel's method to the bomb, modifying it somewhat to assist in making the determination more rapid and better adapted to routine work. The method of calculation of the water formed is easily understood from the following equation:

Weight of water formed $= d - e + f$, in which

d = Weight of bomb after combustion, when it contains combustion gases at 1 atmosphere pressure, — weight of gas in the bomb — weight of nitric acid formed — weight of ash.

e = Weight of bomb before charging with oxygen — weight of air it contains — weight of pellet — weight of ignition thread — weight of kindler (if used).

f = Weight of water leaving the bomb on releasing the pressure.

The percentage of hydrogen is then easily calculated, corrections being necessary for the hydrogen in the ignition thread, in the oxygen (if any is present), in the nitric acid, and in the kindler.

Description of Apparatus Used.

Calorimetric Bomb.—In this research we have employed a Kröker bomb, such as has been used by Jaeger and von Steinwehr,[3] and Fischer and Wrede.[4] The bomb is lined with enamel (although platinum may be substituted) and has a platinum-lined cover, and two valves with platinum-iridium points, one for the admission of oxygen and the other through which compressed air may be admitted to completely drive out the combustion gases if desired. The method of analysis here described is applicable, however, to a one-valve bomb. Instead of igniting the sample by iron wire, we use platinum wire, a cotton thread extending from this platinum wire to the substance to be burned; to ignite the sample, the current is passed through the platinum wire, raising it to incandescence and igniting the thread which, in turn, ignites the substance. A platinum cup is furnished with each bomb, but we find that the platinum deteriorates rapidly and we have therefore substituted nickel capsules;[5] a nickel wire support serves to hold the capsule in place.

---

[1] Langbein, *Z. offentl. Chem.*, 76 (1897).

[2] Hempel, *loc. cit.*

[3] Jaeger and von Steinwehr, *Ber. phys. Ges.*, 5, 353 (1903).

[4] Fischer and Wrede, *Sitzber. K. Preuss. Akad. Wiss.*, 5, 129 (1908).

[5] See Atwater and Snell, THIS JOURNAL, 25, 659 (1903).

Compressed Oxygen.—In all of the more recent experiments we have used Linde oxygen made from liquid air, which is free from carbon dioxide and combustible gases. Analyses made of this gas showed but 6 milligrams of carbon dioxide in 100 grams of oxygen, and we were unable to find an appreciable amount of hydrogen or hydrocarbons.

Balance.—For weighing the bomb in our analyses, we make use of a balance[1] on which one is able to weigh accurately a load of 10 kilograms to 0.01 gram.

Gas Analysis Apparatus.—For our gas analyses, we use the Haldane apparatus, with which analyses of carbon dioxide and oxygen can be made with an accuracy of 1 part in 500. As a compensating burette is used, variations in pressure and temperature of the outer air are without effect. For the finer adjustment of the level of the mercury, a screw pinchcock of special construction is so applied that after closing all communication with the leveling tube, a slight motion of the screw so alters the pressure on the rubber tube as to allow a very accurate adjustment of the mercury in the burette.

Method of Manipulation.

In a determination, the bomb is first cleaned. The substance to be burned is then weighed—with the capsule, if ash is present—and put into the bomb, the ignition adjusted, and the cover screwed on. The valve is opened and then closed to make sure that the interior is at atmospheric pressure and the bomb and contents are weighed to 0.01 gram. The bomb is next charged with oxygen to 20 or 25 atmospheres and again accurately weighed. The combustion follows, the bomb being placed in a calorimeter, if a determination of the heat of combustion of the material is also desired After the combustion, the bomb is carefully dried until it weighs exactly the same as it did before the combustion, so that the weighings taken after the combustion may be upon the same basis as those before.

The gas is released from the bomb, passing through a weighed U-tube containing sulphuric acid, then through the top of two T-tubes connected to two Haldane gas samplers previously filled with mercury, and finally bubbles through water. When the combustion gases have seemingly displaced the air previously in the system, the two gas samplers are filled with the gas by displacement of mercury, the mercury in the sample being lowered by means of a leveling bulb connected to the lower end of the sampler; then the gas in the sampler is put under pressure of mercury by closing the upper stopcock, and raising the leveling bulb on the outside. When the gas in the bomb reaches atmospheric pressure, the bomb is closed and weighed. It is then opened, the ash, if any, is weighed, and the rinsings are titrated for nitric acid. In determining the amount of nitric acid, we use the method of Stohmann, titrating with a solution of sodium carbonate of 0.003706 gram per cc.; 1 cc. of this solution is equivalent to 0.004406 gram of nitric acid, the heat of formation of which is 1 calorie. A table can readily be prepared showing the respective weights of nitric acid, hydrogen and nitrogen which the various volumes of sodium carbonate solution represent. With the analysis of the gas samples for carbon dioxide, all the data necessary for the determination of carbon and hydrogen are at hand.

---

[1] The balance, with glass case, was furnished through the Bausch & Lomb Optical Co., at a duty-free price of about $40.00.

The gas samples, being under pressure, need not be analyzed immediately but may be kept a week or longer, and a number of analyses made at the same time. The value of keeping the samples under pressure lies in the fact that if a slight leak occurs, some of the gas inside may escape, but none from without can enter the sampler. If, however, the gas samples have been kept for some time, they should be tested to find out if they are still under pressure, and if not, they should be discarded. When the analyses of the two samples show a marked difference, the one having the larger percentage of carbon dioxide is taken, as it is assumed that the other has air mixed with it; if the agreement of results is good, an average is taken.

In addition to collecting the sample over mercury, we have allowed the gas from the bomb to flow directly through the gas sampler and eventually displace all the air. To facilitate this displacement, the direction of the flow of gas is reversed during the operation. Duplicate analyses of gas from the same combustion show no differences in the two methods of sampling.

Calculation of Results.—From the data thus obtained, the computation follows. The formula used for computing the weight of carbon is:

$$\text{Weight of carbon} = (c + 0.137a)/(1 + 266.67/b).$$

The three factors, c, a, and b, are derived from the data previously obtained. c (the weight of gas in the bomb at the end of combustion) equals the weight of the bomb immediately after the combustion, less the weight of the bomb after all but 1 atmosphere of the combustion gas has been released, plus the weight of this atmosphere of gas (calculated from the table described later), less the weight of water passed out of the bomb and collected in the sulphuric acid U-tube.

The weight of nitrogen gas in the bomb at the end of the combustion, a, is found by adding the weights of nitrogen in the atmosphere of air in the bomb before the bomb is charged with oxygen, in the oxygen supplied, and in the substance burned, and from this total, subtracting the weight of the nitrogen oxidized to nitric acid. The weight of nitrogen in the air of the bomb before charging is constant for every bomb and is easily calculated from the volume. The weight of the oxygen added to the bomb is equal to the difference between the weights of the bomb before and after charging; the weight of nitrogen in this oxygen is obtained by multiplying the weight of oxygen by the percentage weight of nitrogen it contains.[1] The weight of nitrogen in the sample burned is calculated from a Kjeldahl analysis of the substance; if no Kjeldahl analysis has been made, an estimation of the quantity of nitrogen with an accuracy of 0.10 gram, may suffice, as an error less than this will not affect the percentage of carbon by more than 0.15 per cent.

The percentage of carbon dioxide by volume, *b*, is found with the Haldane apparatus. After the total amount of carbon in the oxygen, in the thread used for ignition, and in the kindler (such as naphthalene or benzoic acid) has been subtracted from the weight of carbon thus found, the percentage of carbon is obtained by dividing the weight of carbon by the weight of the substance. Assuming the cotton thread (0.006 gram) used for ignition is pure cellulose, the carbon in the thread is calculated.

In calculating the percentage of hydrogen, use is made of the following formula:

$$\text{Weight of water formed} = d - e + f.$$

d represents essentially the weight of the bomb proper and the water it contains, and is found by subtracting from the weight of the bomb at the end of a combustion (with the pressure released and but one atmosphere of combustion gases left behind) the combined weights of the nitric acid, of the ash present and of the atmosphere of combustion gases. This latter factor involves a knowledge of the volume of air space within the bomb and the composition of the gas. The volume of the air space in the bomb is a constant and is found by weighing the bomb full of water. The percentage of carbon dioxide is already known, and the percentage of nitrogen (6 to 7 per cent. when no nitrogen is present in the substance) is found to be sufficiently constant to make an analysis for nitrogen unnecessary. A table has been prepared showing the weights of gas occupying this space for the varying percentages of carbon dioxide and nitrogen. When the substance contains considerable nitrogen, the gas may be analyzed for nitrogen on the Haldane apparatus, or it is much simpler and sufficiently accurate to approximate the percentage of nitrogen;[2] this is accomplished by the proportion

$$x : 7 = a : 0.44.$$

In this proportion 7 equals the percentage of nitrogen gas usually obtained when no nitrogen is in the sample, *a* equals the weight of nitrogen gas present (*a* in the formula for determining carbon), and 0.44 equals the weight of nitrogen gas usually present, when no nitrogen is in the substance. The possible error in the percentage of hydrogen from using this formula is very small, an error of 3 per cent. in total nitrogen leading to an error of only about 0.0001 gram of hydrogen. The following table has been calculated for a bomb containing 275 cc. Intermediate values are easily found by interpolation.

---

[1] The percentage of nitrogen by volume is usually supplied by the manufacturer.

[2] With a two-valve bomb, one may sweep the combustion gas from the bomb with air and thus be able to deal with the weight of the bomb full of atmospheric air, instead of combustion gases. This would require more time and also a careful measurement of the water leaving the bomb.

It may be noted that this table is also used in the carbon determination in calculating the weight of gas in the bomb at the end of a combustion.

Per cent. CO_2.	Per cent. O_2.	Per cent. N_2.	Wt. 1 liter of gas. Grams.	Wt. of 275 cc Gram.
12	81	7	1.482	0.4076
14	79	7	1.493	0.4106
16	77	7	1.504	0.4136
18	75	7	1.515	0.4166
20	73	7	1.525	0.4194
12	78	10	1.477	0.4062
14	76	10	1.488	0.4092
16	74	10	1.499	0.4122
18	72	10	1.510	0.4153
20	70	10	1.520	0.4180
12	75	13	1.472	0.4048
16	71	13	1.494	0.4108
20	67	13	1.515	0.4166
12	72	16	1.467	0.4034
16	68	16	1.489	0.4095
20	64	16	1.510	0.4153
12	68	20	1.460	0.4015
16	64	20	1.482	0.4075
12	64	24	1.454	0.3999
16	60	24	1.475	0.4056
..	21	79	1.296	0.3564

e represents the weight of the empty bomb. This is found by subtracting from the weight of the bomb at the beginning of the experiment before charging with oxygen (1) the weight of air which it contains (see table), (2) the weight of the substance burned, and (3) the weight of the ignition thread and kindler.

f is the weight of the water leaving the bomb on releasing the pressure and collected in the sulphuric acid U-tube and has been found to be very constant (0.017 gram). Owing to the small variation in this weight, we have decided that we may safely discard the U-tube and assume the weight of water leaving the bomb to be 0.017 gram.

One-ninth of the weight of water thus found plus the weight of hydrogen in the nitric acid formed, minus the hydrogen in the ignition thread and in the kindler, gives the weight of hydrogen in the substance.

Specimen combustion.
(Nitrogen-free material.)

Cane sugar. Weight taken = 1.3117 grams

Weight of ignition thread	0.006	gram
Weight of bomb before charging with oxygen	2613.30	grams
Weight of bomb after adding oxygen	2621.62	grams
Weight of oxygen	8.32	grams
Weight of bomb after combustion gases are passed out	2612.82	grams
Gas analysis = 17.01 per cent. CO_2 Nitric acid =	0.034	gram
Weight of water leaving bomb on release of pressure	0.017	gram

Weight of gas in bomb at end of combustion with pressure released 0.415 gram (from table).

Weight of air in bomb at start of combustion, 0.356 gram (from table).

Percentage of carbon. Weight of carbon = $(c + 0.137a)/(1 + 266.67/b)$.

2621.62 8.32
—2612.82 ×1.6 per cent. (percentage of nitrogen in oxygen by weight).

8.80 0.1331
+0.415 +0.2737 nitrogen in air in bomb

9.215 0.4068
—0.017 —0.007 nitrogen in nitric acid.

9.198 = c 0.400 = a 17.01 = b

Substituting in this equation:

Weight of carbon = $[9.198 + (0.137)(0.400)]/[1 + 266.67/17.01] = 9.253/16.677 =$ 0.5548 gram.

0.5548
—0.0027 carbon in thread. (No carbon in the oxygen used.)

0.5521 carbon in sugar.
0.5521 ÷ 1.3117 = 42.09 per cent. carbon.

Percentage of hydrogen. Weight of water = $d - e + f$.

2612.82 2613.30
—0.415 —0.356

2612.405 2612.944
—0.034 —1.312 0.017 = f

2612.371 = d 2611.632
—0.006

2611.626 = e

Substituting, weight of water = 2612.371 — 2611.626 + 0.017 = 0.762 gram.

0.762/9 = 0.0847 gram = weight of hydrogen.

0.0847
+0.0005 hydrogen in nitric acid.

0.0852
—0.0004 hydrogen in ignition thread.

0.0848 gram hydrogen in sugar.
0.0848 + 1.3117 = 6.47 per cent. hydrogen.

Specimen combustion.

(Nitrogenous material.)

Urea. Weight taken = 1.9202 grams

Kindled by 0.0583 gram of benzoic acid.

Weight of ignition thread........	0.006 gram
Weight of bomb before charging with oxygen.............	2613 22 grams
Weight of bomb after adding oxygen...........	2620 87 grams
Weight of oxygen........	7 65 grams
Weight of bomb after combustion gases are passed out.....	2612.50 grams

Gas analysis = 14.135 per cent. CO_2. Nitric acid = 0 050 gram

Weight of water leaving bomb on release of pressure. ..... 0 017 gram

Weight of gas in bomb at end of combustion with pressure released 0 404 gram (from table).

Weight of air in bomb at end of combustion 0.356 gram (from table).

Percentage of carbon. Weight of carbon = $(c + 0.137\ a)/(1 + 266.67/b)$.

Gas in bomb contains approximately 21 per cent. nitrogen for:

$x : 7$ per cent. $= 1.29 : 0.44$ $x = 20^1/_2$ per cent.

2620.87
—2612.50

8.37
+0 404

8.774
—0.017

8.757 grams = c

7.65
×1.71 per cent. (per cent. nitrogen in oxygen).

0.1308 nitrogen in oxygen
0.2737 nitrogen in air
0.8967 nitrogen in urea

1.301
—0.011

1.29 grams = a

14.135 = b

Substituting in this equation:

Weight of carbon = $[8.757 + (0.137)(1.29)]/[1 + 266.67/14.135] = 8.934/19.866 = 0.4497$ gram.

Carbon in thread...............	0.0027
Carbon in benzoic acid kindler...	0.401
Carbon in oxygen used..........	0.0235
	0.0663 gram

0.4497
—0.0663

0.3834 gram carbon in urea

0.3834 ÷ 1.9202 = 19.97 per cent. carbon.

Percentage of hydrogen. Weight of water = $d - e + f$

2612.50
—0.404

2612.096
—0.050

2612.046 = d

2613.22
—0.356

2612.864
—1.920

2610.944
—0.058

2610.886
—0.006

2610.880 = e

0.017 = f

Substituting, weight of water = 2612.046 — 2610.880 + 0.017 = 1.183 grams
1.183/9 = 0.1314 gram of hydrogen.

0.1314
+0.0008 hydrogen in nitric acid

0.1322
—0.0033

0.1289 gram hydrogen in urea

0.0004 hydrogen in ignition thread
0.0029 hydrogen in benzoic acid

0.0033

0.1289 ÷ 1.9202 = 6.71 per cent. hydrogen

In a carbon determination, the greatest liability to error rests with the gas analysis. An error of one-third of 1 per cent. in gas analysis should make a similar error of one-third of 1 per cent. in the result. Under the most adverse conditions, one should not make an error of greater than ±0 5 per cent. in these analyses and in the sampling. As the formula involves two weighings of the bomb, allowing each weighing is inaccurate to ±0.01 gram, a maximum error of ±0.02 gram is possible which would ordinarily be about ±0.2 per cent. in the total carbon. Errors from other sources would be so small as to be practically negligible, so that the total maximum error possible is ±0.7 per cent.

The hydrogen determination is liable to a slightly larger percentage error. Two weighings of the bomb being necessary, an error of 0.02 gram of water is possible, involving from 1 per cent. to 5 per cent. error in the hydrogen according to the amount of hydrogen in the substance. All the other data used in calculating the water are sufficiently accurate to involve an error of not more than 1 per cent. One or two features in the analysis for hydrogen require attention: the presence of hydrogen, or hydrocarbons, in the oxygen used will cause the formation of water in the bomb; if an oxygen cylinder contains even as small an amount as 0.02 per cent. of hydrogen by weight, as much as 0.0144 gram of water will be formed when using about 8 grams of oxygen in a combustion, thus introducing an appreciable error. We have tested several cylinders of Linde oxygen and failed to find hydrogen in any of them. Another seemingly apparent difficulty would be the action of oxygen and nitric acid upon the lead gaskets of the bomb. The lead when oxidized would increase in weight and this increase would be measured as water. Practically, it has been found by experiments that the lead gasket, although superficially oxidized, does not appreciably increase in weight; experiments with an aluminium gasket give results parallel to those with the lead, although with the aluminium gasket there is no apparent oxidation during combustion. It is seen that the liability of error in the hydrogen determination varies from 2 to 6 per cent., according to the amount of hydrogen present.

The following determinations give some idea of the fluctuations of the results of this method for determining carbon and hydrogen simultaneously.

		Per cent. C.	Per cent. H.
Sugar	Theory	42.11	6.43
	I	42.06	6.46
	II	42.28	6.42
	III	42.23	6.57
Benzoic acid	Theory	68.85	4.92
	I	68.97	5.00
	II	68.77	5.11
Urea	Theory	20.00	6.67
	I	19.85	6.77
	II	19.96	6.71
Hippuric acid	Theory	60.34	5.03
	I	60.31	4.93

NUTRITION LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON,
VILA ST., BOSTON, MASS.

THE COMPOSITION OF SOME BENGALI FOOD MATERIALS.

BY HOPE SHERMAN AND H. L. HIGGINS.

Received January 24, 1910.

The importance of a knowledge of the dietetic habits of various nationalities was frequently emphasized by the late Professor W. O. Atwater. In connection with an extensive investigation into the food and diet of different classes of people in America, which was instituted by him and carried out under his direction, considerable material was collected regarding the dietetic habits of other nationalities, especially those of the Chinese and Japanese.[1] These data show that many popular impressions regarding the diet of people in foreign countries are erroneous. Particularly is this true with regard to the relative proportions of animal and vegetable food and with regard to the amount of protein ingested.

While considerable information has been gathered concerning the food and diet of Europeans and Americans, with the exception of the publications previously referred to, but a small amount of data is available regarding the dietetic habits of the swarming population of Asiatic countries. Of especial interest, therefore, is an investigation of the highest scientific accuracy as to the food and diet of various classes of people in India, which has been undertaken within the last few years by Captain D. McCay, of the Calcutta Medical College. Captain McCay first studied the dietetic habits of the Bengalis, who are practically vegetarians, living for the most part on rice and dhall (pulse). The results of this study have been published in a memoir,[1] in which Captain McCay points out the noticeable peculiarities in the dietetic customs of the Bengalis, and discusses their bearing upon the physical development and endurance of this class of people.

---

[1] Blasdale, "A Description of Some Chinese Vegetable Food Materials and Their Nutritive and Economic Value," U. S. Dept. Agr., Office Exp. Sta., *Bull.* 68 (1899). Jaffa, "Nutrition Investigations among Fruitarians and Chinese at the California Agricultural Experiment Station, 1899–1901," U. S. Dept. Agr., Office Exp. Sta., *Bull.* 107 (1901); Jaffa, "Further Investigations among Fruitarians at the California Agricultural Experiment Station," U. S. Dept. Agr., Office Exp. Sta., *Bull.* 132 (1903). Oshima, "A Digest of Japanese Investigations on the Nutrition of Man," U. S. Dept. Agr., Office Exp. Sta., *Bull.* 159 (1905).

Inasmuch as the heats of combustion of the typical foodstuffs studied were not determined by Captain McCay, it seemed desirable to secure definite evidence with regard to these values, and arrangements were made by Professor F. G. Benedict, Director of the Nutrition Laboratory, to secure from Captain McCay samples of the food materials used in the investigations. A collection of these samples was sent to the Nutrition Laboratory from India in air-tight cans, and the analyses have been made and the heats of combustion determined by us.

As soon as the samples were received, they were ground and placed in well-stoppered, sealed bottles; determinations were then made of the water, nitrogen, fat, and heat of combustion. All the determinations were made in duplicate, frequently in triplicate, and the results are given in the table herewith.

The water was determined by prolonged desiccation in a high vaccum, according to the method of Benedict and Manning.[2] The nitrogen determinations were made by the Kjeldahl method, which was carefully checked by the determination of nitrogen in pure uric acid. The determinations of the fat were made in a special apparatus designed by Winton. The heat of combustion was determined in a Kröker calorimetric bomb by means of a new form of adiabatic calorimeter, designed by Benedict and Higgins.[3] The hydrothermal equivalent to the calorimeter system was so taken that the heat of combustion of pure cane-sugar was 3959 calories per gram.

For purposes of comparison, the composition of various American food materials, as given by Atwater and Bryant,[4] is included in the table. Thus, wheat and wheat ata (the latter, a flour obtained by grinding wheat) are compared with the ordinary grades of American wheat flour; makkai ata, with corn meal and corn; dhall (pulse), with the dried peas used in this country; and rice, with the ordinary uncooked rice of commerce. Certain determinations which have been made by Captain McCay on these food materials and published by him in the memoir referred to have also been included in the table under the heading "Calcutta analyses."

---

[1] McCay, "Standards of the Urine and Blood and the Bearing of the Metabolism of Bengalis on the Problems of Nutrition," Scientific Memoir No. 34. Issued under the authority of the Government of India by the Sanitary Commission with the Government of India, Simla. Calcutta, 1908.

[2] Benedict and Manning, "The Determination of Water in Foods and Physiological Preparations," *Am. J. Physiol.*, 13, 309 (1905).

[3] Benedict and Higgins, "An Adiabatic Calorimeter for Use with the Calorimetric Bomb," THIS JOURNAL, 32, 461 (1910).

[4] Atwater and Bryant, "The Chemical Composition of American Food Materials," U. S. Dept. Agr., Office Exp. Sta., *Bull.* 28 (1902).

ANALYSES OF BENGALI AND AMERICAN FOOD MATERIALS.

Sample number.	Substance.	Water. Per cent.	Nitrogen. Per cent.	Protein.[1] Per cent.	Fat. Per cent.	Heat of combustion Cals. per g.
	Bengali food materials.					
1	Wheat[2]	10.20	1.96	12.25	2.17	4.010
2	Wheat ata (wheat flour)	9.82	2.33	14.56	3.39	4.093
3	Wheat ata (wheat flour)	10.51	2.02	12.63	2.14	3.949
4	Makkai[2] (corn)	10.00	1.77	11.06	5.03	4.132
5	Makkai ata (corn meal)	9.94	1.52	9.50	4.41	4.057
6	Arar dhall (pulse)	9.70	3.58	22.38	1.51	4.067
7	Arar " "	9.30	3.58	22.38	1.45	4.072
8	Arar " "	7.99	3.65	22.81	1.82	4.110
9	Gram " "	9.00	3.50	21.88	4.81	4.290
10	Gram " "	8.99	3.54	22.13	5.14	4.293
11	Gram " "	9.48	3.82	23.88	5.14	4.274
12	Kalai " "	9.95	3.96	24.75	0.75	4.026
13	Kalai " "	10.43	3.91	24.44	0.88	4.042
14	Massur " "	9.78	4.23	26.44	0.67	4.063
15	Massur " "	10.19	4.42	27.63	0.70	4.056
16	Massur " "	9.80	4.24	26.50	0.80	4.060
17	Mottar " "	9.82	4.22	26.38	0.90	4.041
18	Mottar " "	9.70	4.87	30.44	1.02	4.110
19	Mung " "	9.80	4.09	25.56	0.85	4.051
20	Burmah rice	8.95	1.26	7.88	0.42	3.823
21	Rangoon rice	11.59	1.29	8.06	0.45	3.818
22	Rice (new)	10.82	1.23	7.69	0.19	3.810
23	Rice (old)	10.69	1.19	7.44	0.29	3.801
	Calcutta analyses.[3]					
	Ata	...	....	11.50	2.90	.....
	Arar dhall (husked)	....	....	19.86	3.20	.....
	Massur dhall	.....	....	23.25	2.70	.....
	Rice	.....	....	6.39	0.15	.....
	American food materials.[4]					
	Wheat flour	12.0	....	11.4	1.0	.....
	Corn meal	10.3	....	7.5	4.2	.....
	Peas (dried)	9.5	....	24.6	1.0	.....
	Rice	12.3	....	8.0	0.3	.....

---

[1] Different factors for computing the protein of the various classes of food materials have been proposed by Atwater and Bryant (see Rept. Storrs, Conn., Agr. Expt. Station, 1899, pp. 76-79), but the factor 6.25 was used here in all cases so as to make the results more nearly comparable with those of Captain McCay.

[2] Received whole, and ground for sampling.

[3] McCay: *Loc. cit.*, pp. 34 and 35.

[4] The values for these food materials were taken from *Bull.* 28 of the Office of Exp. Sta., U. S. Dept. Agr. (1902), and represent the average of a large number of analyses.

The samples sent to the Nutrition Laboratory for analysis were taken from the old crop and packed for shipment during the hot, dry season. Captain McCay also analyzed samples of these food materials from the same crop, but the samples were selected earlier in the year when the crop first came upon the market. The results are as yet unpublished but Captain McCay reports that his analyses agree very satisfactorily with those made by us, allowing for the variations in moisture content occasioned by the difference in time of sampling.

Of special interest in the results here shown is the large amount of fat in the wheat ata. The proportion of fat in wheat flour, as commonly used in this country and as shown by some 200 analyses,[1] is from 0.3 to 1.9 per cent., while for the two samples of wheat ata analyzed by us, it was 3.39 and 2.14 per cent. respectively, and 2.90 per cent. as shown by the Calcutta analyses given in the table. The higher percentage of fat will result in a corresponding increase in the heat of combustion. The proportion of fat in the Gram dhall is also high as compared with the other varieties of dhall, being fully three times that shown for any of the others, and the heats of combustion are likewise higher.

NUTRITION LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON,
VILA ST., BOSTON, MASS.

[CONTRIBUTION FROM THE FOOD RESEARCH LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

AN APPLICATION OF THE FOLIN METHOD TO THE DETERMINATION OF THE AMMONIACAL NITROGEN IN MEAT.

BY M. E. PENNINGTON AND A. D. GREENLEE.

Received January 27, 1910.

The quantity of loosely bound nitrogen which occurs in protein-rich tissues such as meat has long been recognized as an indication of the freshness of the substance. Bacteria have been recognized as energetic agents in the decomposition of these protein-rich tissues, with the formation of relatively large amounts of such loosely bound nitrogen.

The methods for the estimation of the quantity of this nitrogen have been far from satisfactory, though the Folin method has served well for its estimation in such substances as urine.

For the estimation of the so-called ammoniacal nitrogen in meat and meat extracts, distillation with magnesium oxide has been the method most used.[2] This method, however, is unsatisfactory in that, even after hours of distillation, small quantities of ammoniacal nitrogen continue to be evolved and the conditions of the experiment, especially the rate of distillation, markedly affect the amount of nitrogen split off. That which is evolved during the first hour, when the rate is 200 cc. of distillate, is usually considerably greater than during subsequent hours, though the succeeding periods—even to the fifth or sixth—yield quantities too large to be disregarded. Such being the case, it would seem probable that the boiling with even a mild alkali causes a progressive splitting of more firmly bound nitrogen compounds that would tend to vitiate the results, because the separation of amine or other forms of nitrogen is apparently gradual rather than sharply marked.

---

[1] Atwater and Bryant, *Loc. cit.*, p. 58.

[2] Richardson, THIS JOURNAL, 30, 1515.

Richardson gives successive distillations, up to ten, on hashed frozen meat—presumably beef—showing that approximately one-third of the total nitrogen obtained is evolved in the first hour, and that after the sixth hour the quantities vary from 0.005 to 0.002 per cent. At no time did he get nitrogen-free distillates. For practical purposes he distils but one hour.

The following table indicates the rate of the evolution of nitrogen by the magnesium oxide distillation method, using 25 grams of chicken meat, 10 grams of magnesium oxide and 450 cc. of water, and distilling at such speed that 200 cc. of distillate collect in one hour. 0.1 *N* sulphuric acid is used to collect the free ammonia.

Table I.—Rate of Evolution of Ammoniacal Nitrogen by the Magnesium Oxide Method.

Description of sample.	Distillation periods, one hour each.	Percentage of nitrogen evolved.	Description of sample.	Distillation periods, one hour each.	Percentage of nitrogen evolved.
No. 299—Fowls of known history in storage two years. In excellent condition.	1	0.036	No. 304—Fowls of unknown history in storage 6 years.	1	0.109
	2	0.013		2	0.021
	3	0.011		3	0.017
				4	0.015
	Total,	0.060		5	0.012
				Total,	0.174
No. 305—Fowl chilled for 48 hours after slaughter at 32° F., then kept at temperature of cool room for 48 hours.	1	0.033	No. 306—Fowl chilled for 48 hours after slaughter at 32° F. Kept at temperature of cool room for 72 hours.	1	0 055
	2	0.020		2	0.023
	3	0.016		3	0.018
	4	.....		4	0.018
	5	0.009		5	0.019
				6	0.016
	Total,	.....		Total,	0.149
No. 308—Fowl chilled for 24 hours after slaughter at 32° F.	1	0.041			
	2	0.019			
	3	0.015			
	4	0.016			
	Total,	0.091			

From the foregoing determination of ammoniacal nitrogen in the flesh of chickens of varying history it would appear that it gives even less satisfactory results by distillation with magnesium oxide than does beef.

Because the determination of this loosely bound nitrogen should be one of the best methods we have for the detection of deterioration in flesh, there has been an endeavor to adapt the method of Folin to such substances, believing that in the cold and with a weak alkali, such as magnesium oxide, there would be a better chance of a sharp separation of ammoniacal nitrogen.

A study of the literature pertaining to the Folin method has shown a scarcity of detail concerning the time required and the strength of the air current. Folin in his original paper[1] states that for urine analysis 600–700 liters of air per hour are required during a period of 1 to 1$^1/_2$ hours. Boussingault in 1850[2] used 56 liters of air per hour for five hours, and found that nitrogen remained. He, therefore, abandoned the method.

Most of the more recent papers, as those of Kober,[3] Gill and Grindley,[4] and Sebellen, Brymeldsen and Haavardsholm,[5] deal with the conditions necessary for the extraction of the ammonium salts from the Kjeldahl digestion rather than from the original tissue or extract.

It seemed desirable, therefore, to attempt the elimination of loosely bound nitrogen from such substances as meat and its extracts by a strong current of air, and to observe the results between the volume of air and the time required for the doing of the work. It has been found that the usual water pump of the laboratory is not adequate. A small air pump, driven by a $^1/_4$ h. p. motor, answers the purpose, and an anemometer, such as is used to measure the volume of air entering mine shafts, etc., records the total volume of air passing through the apparatus. The ingoing air is purified by sulphuric acid in a flask provided with a Hopkins safety bulb. It then passes through a liter flask in which 25 grams of finely-ground meat are suspended in 250 cc. of water, with 5 grams of magnesium oxide. Between this flask and the 0.1 *N* sulphuric acid absorption bottle is an empty 250 cc. flask, to catch any mechanical spattering or frothing; and beyond the acid bottle a 100 cc. flask is placed to catch any particles of the acid that may pass into the exit tube. The flasks are set up in batteries of four, using one brass or glass four-way tube to connect with the air pump, and another of similar form leading to the air wash bottle (see figure on next page).

It has been found that about 30,000 cubic feet of air through the whole system or 8,000 cubic feet through each individual series of flasks, and a period of three to six hours, is sufficient to remove all of the nitrogen which is eliminated by weak alkali at an ordinary temperature When such an

---

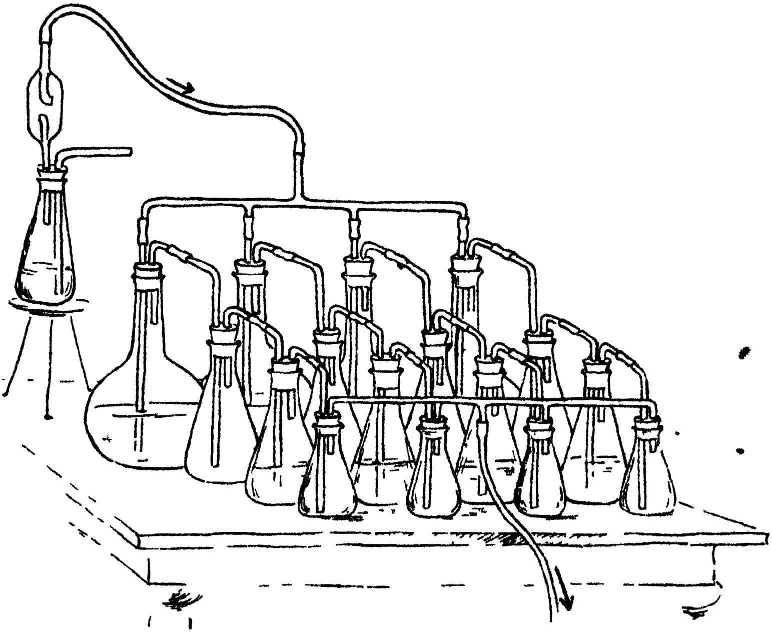
[1] *Z. physiol. Chem.*, 37, 161.

[2] *Memoires de Chemie agricole*, 291.

[3] THIS JOURNAL, 30, 1131.

[4] *Ibid.*, 31, 1249.

[5] *Chem.-Ztg.*, 33, 793.



elimination has occurred the receiving flasks remain free from ammoniacal nitrogen even though a rapid current of air be passed for several additional hours.

The addition of about 25 cc. of alcohol largely prevents the foaming of the protein, which may happen during the latter part of the aspiration period. When once started but little attention is required except an occasional shaking of the flasks. One gram of sodium fluoride, and a temperature of 10–15°, has been found a satisfactory method of preserving unchanged the suspension of meat in water for a period of 24 hours — a fact which is of considerable importance, if many samples are received at one time.

Like the evolution by distillation with magnesium oxide, the preponderance of ammonia is given off during the first hour but, unlike that procedure, there is a steady decrease until the zero point is reached. Table II illustrates the rate of evolution as influenced by the time and the amount of air.

In certain experiments sodium carbonate was used as a hydrolyzing alkali in quantities varying from 0.5 of a gram to 2 grams, side by side with magnesium oxide. It is of interest to note that the evolution of

TABLE II.—RATE OF EVOLUTION OF AMMONIACAL NITROGEN AS DEPENDENT UPON THE QUANTITY OF AIR AND ITS VELOCITY.

Description of sample.	Extraction period	Percentage of ammoniacal nitrogen evolved	Cu ft. of air used.	Time consumed (in hours).
No. 250-A—Fowl in chill room at 32° F. for 24 hours after slaughter.	1	0.0078	1,668	1
	2	0.0034	1,883	1.16
	3	0.0005	1,150	0.83
	4	0.0003	1,235	1
	5	0.0000	1,435	1
	Total,	0.012	7,371	5
No. 250-B — Fowl in chill room at 32° F. for 24 hours after slaughter. Then the meat was ground fine and preserved in a 0.4 per cent. solution of sodium fluoride for 24 hours.	1	0.0025	366	0.75
	2	0.0031	439	0.75
	3	0.0029	460	0.75
	4	0.0015	480	0.75
	5	0.0011	710	0.75
	6	0.0006	525	0.75
	7	0.0004	360	0.75
	8	0.0002	395	0.75
	9	0.0000	415	0.75
	Total,	0.012	4,150	6.75
No. 251-A—Fowl kept in a cool room for six days.	1	0.0095	3,805	1.5
	2	0.0029	2,308	1
	3	0.0014	2,750	1
	4	0.0007	3,670	1
	5	0.0000	3,180	1
	Total,	0.015	15,713	5.5
No. 252—Fowl of known history, two years in storage. Badly gnawed by rats	1	0.0235	2,600	1
	2	0.0070	3,000	1
	3	0.0039	3,025	1
	4	0.0011	3,175	1
	5	0.0006	3,120	1
	6	0.0000	1,660	1
	Total,	0.036	16,580	6
No. 257-A—Fowl of known history, two years in storage. In fair condition.	1	0.0224	3,150	1.16
	2	0.0044	2,800	1.16
	3	0.0011	2,430	1
	4	0.0000	2,750	1.16
	Total,	0.028	11,130	4.48

ammoniacal nitrogen was the same with both reagents. Such findings may be taken as evidence of the sharply differentiated linkage of loosely bound nitrogen in protein, which is certainly increased during bacterial decomposition and probably during enzyme decomposition (Table III).

TABLE III.—EVOLUTION OF AMMONIACAL NITROGEN BY AIR ASPIRATION AND SODIUM CARBONATE.

No. of sample.		Percentage of ammoniacal nitrogen with MgO. 0.5 gr.		Percentage of ammoniacal nitrogen. with Na_2CO_3.	Amount of Na_2CO_3 used.
No. 308		0.012		0.011	$^1/_2$ gram
No. 309		0.011		0.011	1 gram
	Duplicate	0.011	Duplicate	0.011	
No. 310		0.012		0.012	1 gram
	Duplicate	0.012	Duplicate	0.010	
No. 311		0.014		0.014	1 gram
	Duplicate	0.014	Duplicate	0.012	
No. 312		0.016		0.016	2 grams
	Duplicate	0.016	Duplicate	0.016	

A patient endeavor has been made in this laboratory to correlate the ammoniacal nitrogen evolved by the magnesium oxide distillation method with the condition of preservation of the chicken meat. While variations in the amount were visible when wide differences in the flesh were apparent to the sense of sight, odor, etc., small differences for which laboratory data were essential were more frequently confused than clarified by the analytical results.

Though the quantity of nitrogen obtained by air aspiration is always considerably less than is given off in the first hour by distillation, duplicate analyses check closely and individual samples having the same history show similar amounts of nitrogen with a gratifying regularity. Table IV illustrates this point and indicates, also, the variations by the distillation method when examining samples from the same source.

The results tabulated are divided into three groups—(*a*) chickens chilled in dry air at 0° for 24 hours after killing, which is sufficient to completely remove the animal heat; (*b*) chickens of known history preserved in a refrigerator having a temperature of 10–15° for varying numbers of days; (*c*) chickens, generally of known history, preserved hard frozen for varying periods of time.

It will be noted that the perfectly fresh birds show 0.011 to 0.012 per cent. of ammoniacal nitrogen in the tissue; those kept at moderately low temperatures for from 4 to 9 days run from 0.014 to 0.019 per cent.; while cold-stored specimens all more than a year old, show a wide variation in the quantities depending on their condition, but always much higher than the fresh. The ammoniacal nitrogen obtained from the aqueous extract of the tissue is generally a little less than from the tissue itself.

TABLE IV.—QUANTITY OF AMMONIACAL NITROGEN OBTAINED FROM CHICKEN FLESH OF VARYING QUALITY BY FOLIN METHOD.

	Description of sample	Percentage ammoniacal nitrogen evolved	Cu ft of air used	Time consumed (in hours).	Percentage of ammoniacal nitrogen obtained by distilling 1 hour with MgO
A	No. 255—Fowl 24 hours after slaughter, kept in chill room at 32° F. Dry picked.	0.012	10,500	5	.....
	No. 301—Fowl with same history as No. 255.	0.012	8,175	5	0.046
	No. 300—Same as 255.	0.011	4,375	4	.....
	No. 308—Same as 255.	0.012	6,550	4.5	0.041
	No. 309—Same as 255.	0.011	8,100	4.75	.....
B	No. 289–C—Fowl three days in house refrigerator.	0.014	8,302	6	....
	Aqueous extract of No. 289–C.	0.012	8,302	6	.....
	No. 290—Fowl. Hard frozen. In transit four days	0.014	8,900	5	0.036
	No 291—Same history as No. 290.	0.014	8,900	5	0.030
	No. 311—Fowl 24 hours in chill room at 32° F. Six days in house refrigerator.	0.014	6,925	5	0.026
	No. 289–D—Same history as No. 311.	0.014	7,012	5	0.027
	No. 295—Fowl, five days in house refrigerator without previous chilling.	0.016	7,125	5	0.034
	No. 312—Fowl, 24 hours in chill room at 32° F. Seven days in house refrigerator.	0.016	8,080	6	.....
	No. 296—Fowl, 24 hours in chill room at 32° F. Nine days in house refrigerator.	0.016	14,850	6	.....
	No. 287—Fowl, 24 hours in chill room at 32° F. Six days in house refrigerator.	0.017	8,700	6.25	.....
	No. 288—Same history as 287.	0.018	8,700	6.25	.....
	No. 290–B—Fowl hard frozen. Four days in transit. Seven days in house refrigerator.	0.019	8,625	5	0.034
	No. 291–B—Same history as No. 290–B.	0.018	8,625	5	0.029
C	No. 302 — Chicken, cold-stored one year.	0.019	6,700	6	0.048

TABLE IV—(*Continued*).

	Description of sample.	Percentage ammoniacal nitrogen evolved	Cu. ft of air used	Time consumed (in hours)	Percentage of ammoniacal nitrogen obtained by distilling 1 hour with MgO
C	No. 303—Same as No. 302.	0.019	6,700	6	0.030
	No 253—Chicken of known history, two years in storage.	0.027	5,175	3.66	.
	Aqueous extract of No. 253.	0.025	5,175	3.66	. .
	No. 254—Chicken of known history, two years in storage. Slightly gnawed by mice.	0.032	4,820	3.66	.
	No. 256—Same as 254.	0.031	11,130	4.5	. . .
	No. 298—Same as 254.	0.030	7,350	5	. . .
	No. 258—Same as 254.	0.029	5,988	4.25	. . .
	No. 299—Chicken of known history, two years in storage. Excellent condition.	0.023	11,610	8	0.036
	Aqueous extract 299.	0.022	11,610	8	. . . .
	No. 304—Chicken of unknown history in storage six years	0.058	12,978	6	0.109

[CONTRIBUTION FROM THE FOOD RESEARCH LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.]

THE DETERMINATION OF THE ACID VALUE OF CRUDE FAT AND ITS APPLICATION IN THE DETECTION OF AGED FOODS.

BY M E PENNINGTON AND J S HEPBURN.

Received March 3, 1910

During the study of the handling of poultry intended for food, at present under way in this laboratory, it has been found necessary to devise methods for a more accurate estimation of changes in the composition of flesh than have been in common use and which would be sufficiently prompt to permit of the testing of a larger number of samples each day than is ordinarily accomplished with a moderate laboratory force. The acidity of the fat of the chicken has been found to be a sensitive index of the state of preservation of the whole bird. It increases from a very low value in the freshly killed specimen to forty or fifty times the original number, according to the method of preservation and the length of the keeping period. However, the usual procedure for the estimation of the amount of free acid in the fat, that is, extraction with a suitable solvent, drying, etc., was so time-consuming that its use was greatly restricted. It seemed desirable, therefore, to so modify the method that accurate results could be obtained without such an expenditure of time.

It is a common practice in packing-house work to render by a low heat beef or mutton fat and store for commercial purposes. The acid value of such a rendered fat is determined directly in hot alcoholic solution. The rendering of crude fat as a preparation for analysis is mentioned by Dieterich[1] and Pastrovich[2] studying the autohydrolysis of raw tallow rendered it on the water bath with the addition of a few drops of sulphuric acid to decompose the ammonium soaps which had formed in the decomposition. Several washings with hot water freed the fat from excess of mineral acid and it was then dried, weighed, and its acidity determined.

Rendering a fat to free it from enclosing membranes must be carefully done else the heat will cause a splitting, and oxidation must also be considered.

A determination of the amount of water present in the gizzard fat or subcutaneous fat of chickens shows but 5 per cent., or less. This quantity of water, when samples of 10 grams are taken for the determination of the acidity, can be disregarded. The supporting membranes are also a negligible quantity. Accordingly, the fat, both that from the gizzard and from beneath the skin, separated mechanically is ground in a meat chopper and weighed directly into a 250 cc. Erlenmeyer flask. To this is added 50 cc of alcohol which is neutral to phenolphthalein. This dye is then added as an indicator and the whole brought to brisk boiling, preferably on an electric stove which gives an even heat. The hot alcohol dissolves the fat. It is titrated immediately with 0.1 *N* sodium hydroxide, shaking vigorously, until a pink color appears. The color is not permanent. Indeed it fades very rapidly; hence, a color persisting for one-fourth of a minute can be taken as the end reaction. From the amount of sodium hydroxide used the acid value can be calculated or, if the result is to be expressed as free oleic acid, the latter is found by multiplying the acid value by the factor 0.503.

A simultaneous determination of the acidity of the fat by this method and by extraction with petroleum ether according to the official method of the Association of the Official Agricultural Chemists,[3] as modified by this laboratory, namely, using heat with the solvent to ensure thorough extraction,[4] has been made on fat from chickens kept for varying lengths of time after slaughter and from which the animal heat had been removed both by cold air and by water and ice. The acid value has been determined, also, for both gizzard and subcutaneous fat. The results are collected in Table I.

---

[1] *Helfenberger Annalen*, II Bd., II *Dezenniums*, 138 (1897).

[2] *Monatshefte für Chem.*, 25, 335 (1904).

[3] U. S. Department of Agriculture, Bureau of Chemistry, *Bull.* 107, revised 1908.

[4] *Ibid.*, *Bull.* 115, 66.

TABLE I.—COMPARISON OF ACIDITY OF CRUDE AND EXTRACTED CHICKEN FAT.

Number and description of sample.	Gizzard fat.				Subcutaneous fat.			
	Acid value of crude fat.	Acid value of extracted fat.	Per cent. of free acid as oleic. Crude fat.	Per cent. of free acid as oleic. Extracted fat.	Acid value of crude fat.	Acid value of extracted fat.	Per cent. of free acid as oleic. Crude fat.	Per cent. of free acid as oleic. Extracted fat.
No. 194—Near-by farm. Cold-air-chilled	0.89	0.82	0.45	0.41	.	...	....	...
No. 198—Same as No. 194	0.59	0.53	0.30	0.27	0.78	0.54	0.39	0.27
No. 200—Same as No. 194	0.71	0.63	0.36	0.32	0.84	0.46	0.42	0.23
No. 223—Same as No. 194	0.56	0.65	0.28	0.33	0.47	0.69	0.24	0.35
No. 226—Same as No. 194	0.66	0.51	0.33	0.26	0.60	0.66	0.30	0.33
No. 228—Same as No. 194	0.78	0.71	0.39	0.36	0.69	1.08	0.35	0.54
No 230—Market chicken. Water-cooled, ice-packed. Age unknown, but at least 7 days after killing	2.63	0.68	1.32	0.34	1.73	0.53	0.87	0.27
No. 237—Fowl, air-chilled 32° F. for 24 hrs	0.76	....	0.38	....	0.98	....	0.49	...
No. 238—Wet-packed broilers. History unknown	0.83	....	0.42	....	0.54	..	0.27	....
MIXED GIZZARD AND SUBCUTANEOUS FAT.								
No. 295—Near-by farm. Cold-air-chilled	0.70	0.21	0.35	0.11	....	....	....	....
No. 305—Chilled at 32° F. for 24 hours. Kept at lab. temp. for 2 days	1.55	1.27	0.78	0.64	....	....	....	....
No. 302—11 months in cold storage	3.40	2.85	1.71	1.43	...	..	....	....
No. 303—Chicken of known history. In freezer 11 months. Thawed by cool air	3.69	3.63	1.86	1.83	....	....	....	....
No. 298—Chicken of known history. 2 years in freezer	7.32	4.69	3.68	2.36	....	....	.. .	....
No. 299—Same source as No. 298.	7.72	6.56	3.88	3.30	....	....	....	....

It will be observed that the acidity of the crude fat of a chicken chilled in dry air at about 0° C. for 24 hours after slaughter is less than one—generally 0.8, or, reckoned as oleic acid, 0.40 per cent. A comparison of the values obtained from the same fat after extraction shows either absolute agreement or a close duplication so long as the fat has not aged.

When the fat ages the acidity of the crude material is frequently higher than when extracted by petroleum ether. In a few cases the crude fat has been found to give a lower figure than the extracted. Be the comparative values higher or lower, agreement is uncommon, as is indicated in the latter part of Table I.

In the fresh chicken the acid value of the gizzard fat is generally a little less than that of the subcutaneous fat. It may occasionally be very slightly higher. Even so, the acidity of the fat from the two sources is, in the fresh condition, nearly the same.

As the fat ages, it increases in acidity, whether at a temperature below the freezing point, at the temperature of the usual packing-house chill room or the housewife's refrigerator. This increase is pronounced long before the usual signs of deterioration become manifest and for that reason it is of value as a gauge of incipient decomposition.

TABLE II.—CHANGES IN THE ACIDITY OF CRUDE CHICKEN FAT UNDER VARYING CONDITIONS.

	Gizzard fat.		Subcutaneous fat.	
Number and description of sample	Acid value	Per cent of free acid as oleic.	Acid value.	Per cent. of free acid as oleic.
No 231—Broilers, dry-air-chilled for 24 hours. 24-hr. haul	0.95	0.48	.	..
No. 231(*a*)—Same lot after keeping 4 days at 32°	2.10	1.06	.	...
No 231(*b*)—Same lot after 12 days at 32° F	4.74	2.38		
No. 232—Same shipment as No. 231, but water-chilled and ice-packed	0.88	0.44	.	.
No 232(*a*)—Same lot after 4 days in cracked ice	4.57	2.30	...	.
No. 232(*b*)—Same lot after 7 days in cracked ice.	4.71	2.37	..	..
No. 233—Fowl, same history as No. 231. Kept at 32° F for 8 days	1.65	0.83	1.16	0.58
No 233(*a*)—Same lot after 12 days at 32° F	2.41	1.21	1.51	0.76
No. 234—Fowl, same history as No. 232. Kept in cracked ice for 8 days	4.55	2.29	2.12	1.07
No. 234(*a*)—Same lot after 10 days in cracked ice.	8.86	4.46	2.48	1.25
No. 235—Fowl, air-chilled at 32° F. and kept in chill room 3 days	0.80	0.40	0.88	0.44
No. 235(*a*)—Same lot after 6 days in chill room	1.41	1.71	1.05	0.53
No. 236—Fowl, water-cooled, ice-packed and kept in ice three days	2.20	1.11	2.09	1.05
No. 236(*a*)—Same lot kept 6 days in cracked ice	2.70	1.36	1.26	0.63
No. 237—Fowl, air-chilled at 32° F. for 24 hours	0.76	0.38	0.98	0.49
No. 237(*a*)—Same lot after two days at 32° F.	0.87	0.44	0.83	0.42
No. 218—Fowl from near-by farm. Kept in house refrigerator 3 days	2.18	1.10	1.47	0.74
No. 240—Air-chilled, dry-packed broilers. 2 days railroad haul in refrigerator car	2.47	1.24	.	....
No. 192—Market chicken, not salable	5.99	3.01	...	....
No. 191—Market chicken, no history. Low quality, not fit for sale	6.02	3.03	...	....
No. 193—Market chicken. Stale when purchased. Kept at room temperature for 5 days. Advanced putridity	25.54	12.85	....	....
MIXED FAT.				
No. 284—Just killed when purchased. Kept 6 days in house refrigerator	**1.60**	**0.80**	....	....

Table II shows the acid value of the crude fat of fowls of varied history. In a number of cases several analyses have been made of the same lot of fowls at different periods. These experiments show a progressive increase in the acid value as the time lengthens, and they also show that the more perfect the prompt removal of the animal heat, the lower the acidity. The figures are also sufficiently delicate to show the difference between birds dry-air-chilled, and chilled with water and ice, all other conditions being the same. This fact is of service in determining the best methods for the handling of poultry intended for food and is being used in the examination of market poultry dressed and transported and stored in various ways.

It has been stated that in the fresh chickens the subcutaneous fat tends toward a slightly higher acidity than does that of the gizzard. In the aging chicken, on the contrary, the visceral fat is distinctly more acid and is a better indicator of the condition of the rest of the bird.

Conclusions.

The acidity of the crude fat of chickens is an excellent indicator of their freshness. The results obtained on the crude material are more reliable than after extraction with fat solvents. The acidity of the visceral fat increases with length of keeping time or bad handling more markedly than does the subcutaneous fat.

NEW BOOKS.

The Fundamental Principles of Chemistry. *An Introduction to All Textbooks of Chemistry.* By WILHELM OSTWALD. Authorized translation by HARRY W. MORSE. 341 pp. Longmans, Green & Co. Price, $2.25.

This book is a departure from conventional standards, but readers who are familiar with the author's writings will recognize that it is a natural development of ideas which he has long been known to hold. A chemistry has been worked out "in the form of a rational scientific system without bringing in the properties of individual substances." The fundamental concepts and principles of the science are presented in a logical order and "as free as possible from irrelevant additions." The author considers that the development of the methodical side of chemistry has been greatly retarded on account of the fundamental error of using hypothetical assumptions as an aid to experimental work. The end sought "is the discovery of final truths and the relations between them,—. This does not mean the setting up of analogies and hypotheses, but the careful analysis of concepts and indication of the general facts of experience from which they are derived."

The selection of material and the order in which it is presented is shown by the following list of chapters:

I. Bodies, substances, and properties. II. The three states. III. Mixtures, solutions, and pure substances. IV. Change of state and equilibrium. The equilibria (*a*) liquid-gas, (*b*) solid liquid, (*c*) between the three states, and (*d*) solid-solid. V Solutions. VI. Elements and compounds. VII. The law of combining weights. VIII. Colligative properties. IX. Reaction velocity and equilibrium. X. Isomerism. XI. The ions.

A striking feature of the book is the simple and successful development at a very early stage of the phase rule and of methods of graphical representation. One-component systems are treated in a comprehensive manner in Chapter IV, and a more general conception of the phase rule is given in V in connection with two-component systems. In Chapter VI there is presented a new method of representing in a line diagram the composition of a two-component system at constant temperature and pressure. When composition is plotted in a horizontal direction, the field of existence of each phase may be represented by a single horizontal line. Gas, liquid, and solid phases are distinguished by using dotted lines, ordinary lines, and heavy lines, respectively. The overlapping of two lines represents the co-existence of two phases.

The treatment of chemical processes in the narrower sense, and the definition of elements are dealt with in Chapter VI, and are introduced by a discussion of hylotropy and the methods of identifying a pure substance. The value of the phase relations in deciding whether a compound is formed in a binary system is determined by making a systematic classification of all possible combinations of phases, and of the new combinations obtained when a compound is formed. In this chapter, also, a proof is given of the law of constant proportions with which two substances (elements or compounds) combine to form a compound pure substance; and upon this law is based (Chapter VII) the law of combining weights, and the proof of the law of rational multiples.

In a book of this nature it is not to be expected that the readers will in all cases agree with the author's method of treatment. Many will object to the tacit treatment of the atomic theory as an "irrelevant addition" to chemistry. Some may question the validity of the "law of nature" relating to the formation of metastable substances (page 92): "Those forms appear first which are more stable than the form just left, but which are the least stable among all the possible stable forms."

It is evident at once, from the nature and scope of the book, that the sub-title is somewhat misleading. The author, however, does not expect this book to be used by a beginner. He is in fact "quite of the opinion that a close personal acquaintance with a considerable number of important and characteristic substances is and always must be the fundament of all instruction in Chemistry."

This book will be of great value to the teacher, and to every chemist who has attempted to examine for himself the basis of laws and theories frequently accepted as established or self-evident. W. C. BRAY.

Elementary Modern Chemistry. By WILHELM OSTWALD, Emeritus Professor of Chemistry in the University of Leipzig and HARRY W MORSE, Instructor in Physics in Harvard University. x + 291 pages. Ginn & Company. Price, $1 00.

A text-book in elementary chemistry written by a former professor of chemistry in one of the great German universities in collaboration with an instructor in physics in one of the great American universities would naturally command the attention of those engaged in teaching this subject. While there is a general belief, perhaps more or less unwarranted, that it is a difficult undertaking for one not engaged in teaching chemistry under the conditions which exist in secondary schools to write a text on that subject, nevertheless it is always of great interest to learn the views of others, especially of one whose achievements in chemistry have gained for him the Nobel prize. The nature of Ostwald's "die Schule der Chemie" published in 1903 would naturally lead one to believe that his ideas upon the methods of teaching elementary chemistry were entirely different from the methods in general use in the United States. In Ostwald and Morse's text, however, no such extremely radical difference from prevailing methods is to be found. In general the book not only looks, but for the most part reads, like many of the well known modern texts on elementary chemistry. Since one of the authors is a physical chemist and the other an instructor in physics, naturally the subject is approached from a physico-chemical standpoint. For example, the subject of "phases" is introduced in the first chapter (page 5) and is followed in the text by other physico-chemical conceptions. Accordingly one looks in vain for any mention of such old and familiar terms as "physical" and "chemical changes." Even the term "valence" is conspicuous by its absence.

As was to be expected the subject is presented in an attractive form. While the text proper contains only 278 pages, printed in large type and including nearly 200 experiments and one hundred figures, it contains a fairly comprehensive discussion of such fundamentals of chemistry as the average student can grasp. More attention is devoted to the general laws and less to the application of chemical processes than is generally customary in an elementary text. The book would be of little value except when used under the direction of a competent teacher well versed in the modern conceptions of chemistry. With such a person as a teacher it should prove an acceptable one for students who expect to continue the subject. WILLIAM MCPHERSON.

Recent Advances in Physical and Inorganic Chemistry. By A. W. STEWART, D.Sc., with an Introduction by SIR WILLIAM RAMSAY, K.C.B., F.R.S. With diagrams. Longmans, Green, and Co., 1909. Price, $2.50.

The book contains chapters of a dozen pages or so on some hydroxylamine derivatives (nitroxyl), reactions in liquid ammonia (Franklin's work), the fixation of nitrogen (production of nitrogen oxides, amines, cyanides, nitrides), colloids, elements of the rare earths (with a discussion of their position in the periodic system), and the inactive gases (including a history of their discovery).

More space—from thirty to fifty pages each—is devoted to cobalt-ammines, absorption spectra, atomic weights, double salts and the oceanic salt deposits, and radioactivity.

The essays are interesting and well written, and the author does not hesitate to express his own opinions when occasions arise. He stands for purposive research, not that of "investigators who photograph spectra apparently with no idea beyond finding out what the absorption curve looks like," or that of the organic chemists who "apply somebody else's reaction to the iso propyl derivative when the lower members of the series have already been made." Theories, he thinks, should be capable of being tested, and not "mere verbiage and an excuse for dodging round a dialectic corner as soon as people begin to look into the subject."

The book might well find a place in the reading prescribed for advanced students of chemistry; its one weak point seems to be the chapter on Double Salts, which needs very careful revision. W. LASH MILLER.

RECENT PUBLICATIONS.

ADAMS, W : **Hints on Amalgamation and the General Care of Gold Mills.** Mining and Scientific. 12°, $2.00.

BINZ, DR. A.: **Kohle und Eisen. Aus Wissenschaft und Bildung. Einzeldarstellung aus allen Gebieten des Wissens.** Herausgegeben von Dr. P. Herse. Leipzig: Quelle & Meyer. 8°, 136 s., 1.25 M.

BOUCHONNET, A.: **Industries du plomb et du mercure. Bd. I. Métallurgie.** Paris: O. Doin & Sons. 300 s.

DURKEE, FRANK W.: **Experiments in General Inorganic Chemistry.** 2d ed. rev. Tufts College, Mass.: Tufts College Press. 60 pp., $.50.

FEIT, W.: **Über die Darstellung des Chlorkaliums aus Hartsalz.** Halle: W. Knapp. 8°, 83 s, 2.40 M.

FERNAU, A.: **Praktische Pharmazie.** Wien: F. Deuticke. 2.50 M.

FOOT, F. N.: **Baking Powder and Other Leavening Agents.** New York: Spice Mill Pub. Co. $1.50.

FRIESE, W.: **Tabellen zur Ermittelung der freien Saüre, sowie der flüchtigen und nichtflüchtigen Saüren im Wein.** Dresden: Zahn & Jaensch. 1.50 M.

GERLACH, V.: **Physiologische Wirkungen der Benzoesäure und des benzoesäuren Natrons.** Wiesbaden: Heinrich Staadt. 8°, 95 s, 5 M.

GETMAN, F. H.: **An Introduction to Physical Science.** New York: John Wiley & Sons. 940 pp. $7.50.

Goettler, H.: **Praktische Destillateur-Kursus.** Neustadt a Hdt: D. Meininger. 8°, 99 s., 2 M.

Goldberg, I., und Friedmann, H.: **Die Sulfosäuren des Anthrachinons und seiner Derivate.** Berlin: Weidmannsche Buchhandlung. 3 M.

Haimovici, E.: **Der Eisenbetonbau.** 245 Bändchen der Sammlung "Aus Natur und Geisteswelt." —Leipzig: B. G. Teubner. 131 s, 1.25 M.

Hausbrand, E.: **Hilfsbuch für den Apparatebau.** 2 Aufl. Berlin: J. Springer. Geb. 3.6 M.

Herz, W.: **Der Verteilungssatz. Mit einer Zusammenstellung der wichtigsten Verteilungskoeffizienten zwischen flüssigen Schichten.** (Sonderausgabe aus Bd. XV der Sammlung chem. und chem.-techn. Vorträge), Stuttgart: Ferd Enke.

Jahr, H.: **Anleitung zum Entwerfen und zur Berechnung der Standfestigkeit von Fabrikschornsteinen aus Mauerwerk, Eisen und Eisenbeton, nebst den hierüber erlassen Bestimmungen und die rauchfreie Verbrennung bei Dampfkesseln.** Hagen, i W.: O. Hammerschmidt. 8°, 153 s, 3 M.

Jenke, Dr. F.: **Die volkswirtschaftliche Bedeutung des künstlichen Indigos.** Karlsruhe i Baden: G. Braunsche Verlag. 2.60 M.

Leach, A. E.: **Food Inspection and Analysis.** 2d. ed. New York: John Wiley & Sons

Lunge, G.: **Coal Tar and Ammonia.** 4th ed. 2 Bd. London: Gurney & Jackson. 8°, 1212 pp. 42 s.

Lunge, G.: **The Manufacture of Sulphuric Acid and Alkali, with the Collateral Branches.** 3rd ed. Vol. 2, Parts 1 and 2. London: Gurney and Jackson. 8°, 1042, pp. 42 s.

Nikaido, Y.: **Beet-Sugar Making and Its Chemical Control.** Easton, Pa.: Chemical Pub. Co.

Orthey, M.: **Die Metallhüttenchemie.** Wien: F. Deuticke 15 M.

Peckham, S. F.: **Solid Bitumens.** Spon. 8°, 21 s.

Plato, F.: **Tafel zur Umrechnung der Volumprozente in Gewichtsprozente und der Gewichtsprozente in Volumprozente bei Branntweinen. Berechnet nach den amtlichen Zahlen der Kaiserlichen Normal-Eichungskommission.** 3 Aufl. Berlin: J. Springer. 1 M.

Poulsen, A.: **Cement in Sea Water.** Spon: 8°, 3 s.

Rippel, J.: **Grundlinien der Chemie für Oberrealschulen. 1 Teil: Anorganische Chemie.** 2 Aufl. Wien: F. Deuticke. 264 s., 3 M.

Roschke, K.: **Über α-Oxolaktame.** Hildesheim: August Lax. 51 s., 1.50 M.

Schroeder, Joh. v.: **Zur Kenntnis des Gerbprozesses.** Dresden: Th. Steinkopff. 8°, 1.50 M.

Sidersky, D.: **La réfractométrie et ses applications pratiques.** Paris: Gauthier-Villars. 172 s.

Trnka, R.: **Die physikalischen Eigenschaften des Bodens.** Prag: 24 s.

Tutton, A. G. H.: **Crystalline Structure and Chemical Constitution.** London: Macmillan & Co.

Wadsworth, M. E.: **Crystallography: An elementary manual for the laboratory.** Phila.: J. J. McVey. 299 pp. $3.00.

Wieland, H.: **Die Knallsäure.** (Sonderausgabe aus Bd. XLV der Sammlung chem. und chem.-techn. Vorträge). Stuttgart: F. Enke. 2.40 M.

Zetzsche: **Mikrophotographischer Atlas der industriellen Faserstoffe.** Kötzschen-broda-Dresden. H. F. A. Thalwitzer. 1.50 M.

VOL. XXXII. MAY, 1910. No. 5.

THE JOURNAL

OF THE

American Chemical Society

ON THE OXALATES OF HYDRAZINE.

By J. W. TURRENTINE.

Received March 3, 1910

In 1889[1] Curtius made mention of the formation of an oxalate of hydrazine obtainable by heating triazoacetic acid with a saturated, aqueous solution of oxalic acid. The product was described as a substance crystallizing in small, glistening plates, soluble in water. No attempt was apparently made to ascertain whether the substance was a monoxalate or a dioxalate of hydrazine, and no analytical data whatever were published.

The purpose of the present investigation has been the preparation and study of the two oxalates of hydrazine, $(N_2H_4)_2H_2C_2O_4$ and $N_2H_4.H_2C_2O_4$. It has been thought possible, moreover, that the decomposition of these substances, especially in view of a probable ring structure of the dioxalate, might yield some interesting results.

Hydrazine Monoxalate.

Method of Preparation.—An aqueous solution of this substance was prepared by treating 10 cc. of a 73 per cent. solution of hydrazine hydrate, with 9.18 grams of oxalic acid dissolved in a small amount of water. The solution was filtered and after evaporation on the water bath to the point of saturation was allowed to cool, with the result that a large quantity of minute crystals was obtained. The crystals were first drained on filter paper and were then dried to constant weight in a desiccator over calcium chloride.

Method of Analysis.—Weighed samples of the dried crystals were dissolved in water and the solutions were made strongly alkaline with ammonium hydroxide. They were then heated to boiling and an excess of a solution of calcium chloride, containing 25 grams per liter, was added slowly and with constant stirring. After the precipitates had been allowed to subside, they were filtered and were thoroughly washed with hot water.

---

[1] Curtius and Jay, *J. prakt Chem.*, 39, 27–59 (1889).

In order to avoid the error arising from the possible presence of calcium carbonate in the calcium oxalate thrown down by this method, the precipitates were dissolved in hot, dilute sulphuric acid, and the oxalic acid was determined by titration with a standard solution of potassium permanganate.

The results obtained in four determinations indicate the ratio, mols. N_2H_4 : mols. $H_2C_2O_4$ to be (1) 2 : 1.02; (2) 2 : 1.00; (3) 2 : 0.99; (4) 2 : 0.99. Theory, 2 : 1.00. The average of these results, calculated to a percentage basis, is as follows $H_2C_2O_4$ found, 58.60 per cent.; theory for $(N_2H_4)_2.H_2C_2O_4$, 58.44 per cent.

Three analyses of the monoxalate by the permanganate method described in detail in a subsequent paragraph show the ratio, mols. N_2H_4 : mols. $H_2C_2O_4$ to be (1) 2 : 0.99; (2) 2 : 0.98; (3) 2 : 1.00. Theory, 2 : 1.00. The average of the three results, calculated to percentage of N_2H_4, gave N_2H_4 found, 41.45 per cent. Theory, 41.59 per cent.

Properties.—Hydrazine monoxalate is a white substance that crystallizes from aqueous solution in the form of very fine needles and plates. When the attempt is made to recrystallize the compound, an amorphous substance is frequently obtained in the form of a jelly, which, on evaporation, becomes hard and opaque.

The monoxalate is extremely soluble in water, as shown by the results obtained in the following series of solubility determinations made at 35°. One gram of water at this temperature was found to dissolve (1) 2.003, (2) 1.998, and (3) 2.018 grams, or an average of 2.009 grams of the salt.

Three determinations of the solubility of this compound in absolute alcohol at a temperature of 21.9° showed that it was practically insoluble, or that 1 cc. of alcohol dissolved about 0.0003 gram. The substance is also insoluble in ether. No appreciable residue was left after the evaporation of a small portion of ether that had been shaken with the salt at intervals for several hours. In the case of both alcohol and ether, the liquid was heated to its boiling point in the presence of the salt, and was allowed to come to constant temperature, with frequent shaking, in a thermostat.

No definite melting point is shown by the monoxalate, which in this respect is similar to many other hydrazine compounds. At a temperature of 130° (±2°) it begins to decompose, although even at lower temperatures some indication of incipient fusion is obtained. Above this temperature the compound is eventually transformed into a clear liquid, whether the substance be heated in an open or in a closed capillary tube.

When this liquid is allowed to cool it solidifies, yielding a product that melts at 150° (±2°).

Decomposition.—The decomposition of hydrazine monoxalate was studied under four different sets of conditions, as follows: (1) On a platinum plate in the open air; (2) in an open glass tube; (3) in an atmosphere of hydrogen; (4) *in vacuo*, with a view to the analysis of the evolved gases.

(1) When crystals of the monoxalate were heated on a platinum plate in the open air they fused and boiled, assuming a yellow color. This color gradually deepened to a brown and finally to a black, as the charring of the substance progressed. Throughout the decomposition there was a visible evolution of fumes. Whenever the rate of heating was sufficiently rapid the substance took fire and burned with a blue flame of carbon monoxide.

(2) This experiment was performed in order that the fumes noted in Exp. 1 might be partially condensed and examined. A portion of the substance which had been dried to constant weigh' at a temperature of 100–5° was gradually decomposed. by heating, in an open glass tube. Essentially the same phenomena were observed to take place in the same sequence as in Exp. 1. The vapor which escaped from the tube, as well as that which condensed on the walls, gave a distinct alkaline reaction to red litmus and emitted the odor of hydrazine hydrate. Later in the decomposition the odor of a cyanide was detected, and before the presence of that substance was suspected, symptoms of cyanide poisoning were experienced.

(3) A third experiment was designed with a view to the collection of decomposition products absorbed in acid or in alkaline solution. The decomposition was effected in an apparatus consisting of a glass distilling flask, provided, in lieu of a stopper, with a glass tube sealed in the neck, and extending perpendicularly nearly to the bottom. The side arm of the flask was fused to a Muencke gas wash bottle, containing dilute sulphuric acid. A similar bottle connected to the first and contained carbon-dioxide-free potassium hydroxide.

A stream of hydrogen, purified with the aid of alkaline permanganate, soda lime, and concentrated sulphuric acid, was employed in sweeping the uncondensed products of decomposition into the gas wash bottles.

About one gram of the oxalate was placed in the flask and the air in the entire apparatus was displaced by hydrogen. The compound was then slowly heated to decomposition. At the end of the experiment a small amount of carbon remained in the flask.

An appreciable amount of ammonia and a small quantity of hydrazine were found in the first wash bottle. The alkaline solution in the second bottle was found to contain a small amount of carbonic acid and a considerable quantity of hydrocyanic acid, as shown by both the Prussian blue and the sulphocyanate tests.

During the early stages of the decomposition a liquid condensed on the walls of the neck and side arm of the flask. In Exp. 2 this liquid was shown to be in part, at least, hydrazine hydrate. Two drops of the condensate were subjected to analysis for hydrazine by the method of Rimini.[1] The results obtained when calculated to hydrazine hydrate gave a concentration of 9 per cent. It is probable, however, that the liquid contained in solution compounds of hydrazine other than the hydrate.

The most conspicuous of the substances produced by the destructive distillation of the monoxalate was a white crystalline sublimate deposited on the cooler parts of the flask and of the decomposing substance itself. When a drop of the aqueous solution of this sublimate was evaporated under the microscope, glistening needle-shaped crystals separated out. These crystals were found to contain no carbonic, hydrocyanic, or oxalic acid, and were shown to be capable of reducing acidified potassium iodate in the cold. When the solution from which the hydrazine had been removed by oxidation was subjected to the microchemical test for ammonia with chloroplatinic acid, negative results were obtained. When heated on a platinum plate the substance decomposed, leaving a residue of carbon, thus indicating the presence of organic matter

(4) The decomposition was effected under such conditions that all gaseous products unabsorbable by sulphuric acid or potassium hydroxide could be collected for analysis, uncontaminated by air. The apparatus employed in this experiment was constructed as follows:

To the capillary tip of a Hempel gas burette was joined, by means of a short section of rubber tubing, a Y-tube, one arm of which was closed by a piece of narrow-bore rubber tubing provided with a screw clamp and a tightly fitting glass plug. To the other arm was sealed a glass stop-cock. A section of glass tubing, 0 5 cm. internal diameter and 19 cm long, designed as the container for the substance which was to undergo decomposition, was closed at one end and was sealed to the tube bearing the glass stop-cock. It was then bent so as to extend horizontally outward and in a plane perpendicular to that occupied by the glass Y. It was necessary, of course, in each case to place the compound which was being studied in the tube designed as its receptacle before the fused joint was effected. The burette was filled with mercury. By alternate raising and lowering the level tube of the burette and by suitable manipulation of the valves of the Y-tube, the pressure in the tube containing the sample was reduced to less than 1 mm.

A sample of the hydrazine monoxalate weighing 0.2128 gram yielded about 35 cc. of gas when decomposed in the apparatus just described.

---

[1] Rimini, *Gaz. chim. ital.*, **29**, I, 265–9 (1899); *Chem Zentr.*, **1899**, II, 455.

Of this gas, a volume of 25.8 cc. was passed successively into Hempel pipettes containing potassium hydroxide, alkaline pyrogallol, and ammoniacal cuprous chloride. The contraction observed in the first case was 3.0 cc., corresponding to 11.6 per cent. of gases absorbable in potassium hydroxide. Only a trace of oxygen was found. The contraction noted after treatment with ammoniacal cuprous chloride was 4.5 cc., corresponding to 17.4 per cent. of carbon monoxide.

The residue, 18.3 cc. in volume, was non-inflammable, and was therefore taken as nitrogen; this volume represented 70.9 per cent. of the whole.

A summary of the results of the above experiments shows that the monoxalate of hydrazine is quite unstable at moderately high temperatures and on decomposing yields water, ammonia, hydrocyanic acid, probably in combination, hydrazine, carbon dioxide, carbon monoxide free nitrogen and carbon. An unidentified and more complex compound of hydrazine is found and appears as a white, crystalline sublimate. This compound is being subjected to further investigation.

Hydrazine Dioxalate.

Method of Preparation.—The dioxalate of hydrazine was prepared by adding, drop by drop, to a hot, concentrated solution of oxalic acid, containing 11.02 grams $H_2C_2O_4$ $2H_2O$, 6 0 cc. of a 73 per cent. solution of hydrazine hydrate containing 4 4 grams $N_2H_4.H_2O$. Before the last of the hydrate had been added to the solution of the acid, brilliant crystalline flakes began to appear. The solution was heated, with stirring, until these had redissolved. Then, on cooling, a large mass of beautiful, glistening crystals was obtained. These were filtered by suction, were washed rapidly in cold, distilled water, also with the aid of suction, and were then dried in the open air.

Analysis.—Three samples of this compound, previously dried in an air bath for one-half hour at a temperature of 100–8°, were analyzed for oxalic acid by the calcium chloride precipitation method, outlined above under the analysis of the monoxalate.

The result obtained in three determinations showed the ratio between the molecules of hydrazine and oxalic acid to be (1) 1 : 1.00; (2) 1 : 1.01; (3) 1 : 0.98; theory, 1 : 1. When calculated to a percentage basis the average of these results is: $H_2C_2O_4$ found, 73.63 per cent.; theory, calculated for $N_2H_4.H_2C_2O_4$, 73.60 per cent.

The principal methods so far proposed for the determination of the hydrazine radical in compounds of that substance involve reactions in which that radical undergoes oxidation. Rimini[1] prescribed the use of potassium iodate in acid solution, adding a measured excess of the iodate and titrating the excess with thiosulphate, after reduction with potassium iodide. Petersen[1] employed potassium permanganate in acid solution, as did also Roberto and Roncali,[2] while Sebanejeff[3] used the same oxidizing agent in alkaline solution. He determined the hydrazine radical in an inorganic salt by adding an excess of that reagent and titrating back with arsenious acid.

---

[1] Rimini, *Loc. cit.*

These methods do not lend themselves readily to the analysis of the oxalates of hydrazine on account of the peculiar fact that both the basic and the acid radicals in this compound are strong reducing agents and both react with the oxidizing substances prescribed. This consideration debars the use of the methods of Rimini, of Petersen and of Roberto and Roncali. The use of permanganate in alkaline solution as outlined by Sebanejeff might be employed with modification, as permanganate is not reduced by oxalic acid in alkaline solution, but this procedure would involve a tedious titration with arsenious acid. To acidify the solution for this titration would result in the immediate reduction of the excess of permanganate by the oxalic acid. In the alkaline solution which is therefore required, a voluminous precipitate of manganese compound forms which must be allowed to settle before any color change can be detected in the solution. Moreover, the presence of oxalic acid might interfere in the titration by reducing the arsenic acid[4] then formed, though it is doubtful whether this reduction could occur in an alkaline solution.[5]

These considerations made it necessary to devise a method of analysis which would take into account the reducing action of both radicals of the oxalates and which would therefore permit the simultaneous determination of both hydrazine and oxalic acid. The method of Rimini, which is the most satisfactory for the determination of hydrazine, could not be adapted to this purpose, for while potassium iodate oxidizes oxalic acid, the reaction is too slow,[6] even in hot acid solution, to admit of titration. Potassium permanganate, it has been shown by Browne and Shetterly in their studies on the oxidation of hydrazine,[7] does not oxidize hydrazine in acid solution quantitatively to nitrogen and water, but yields varying amounts of hydronitric acid and ammonia. Methods based on the use of this reagent in acid solution are therefore unreliable. Likewise, in alkaline solution, if the permanganate be added slowly, small amounts of these products are formed. On the contrary, if an excess of the permanganate is added at once in alkaline solution, the amounts of hydronitric acid and ammonia formed are negligible.[1]

---

[1] Petersen, *Atti accad. Lincei*, [5] 15, II, 320–5 (1906), *Chem. Zentr.*, 1906, II, 1662.

[2] Roberto and Roncali, *Industria chimica*, 6, 178 (1904); *Chem. Zentr.*, 1904, II, 616

[3] Sebanejeff, *Z anorg. Chem.*, 20, 21–9 (1889).

[4] Prescott and Johnson, "Qualitative Chem. Analysis," 5th Ed., p. 257.

[5] Naylor and Braithwaite, *Pharm. J. and Trans.*, 13, [3] 464 (1883).

[6] Guiard, *J. Chem Soc.*, 36, 593 (1879).

[7] Browne and Shetterly, THIS JOURNAL, 31, 221 (1909).

In the light of these facts a method of analysis was devised in which the hydrazine was oxidized by permanganate in alkaline solution, and the oxalic acid by more permanganate in the same solution after acidification.

Essentially the following procedure was adopted: The sample to be analyzed was dissolved in water in an Erlenmeyer flask and was treated with 10 cc. of a 4 *N* solution of sodium hydroxide. An amount of standard permanganate solution sufficient to oxidize the hydrazine completely, but not enough to oxidize all of the oxalic acid, was then added and the solution was acidified by adding 5 cc. of concentrated sulphuric acid. After the solution had been warmed until the oxides of manganese had gone into the solution, a clear, colorless liquid remained. Potassium permanganate was then added, drop by drop, until the faintest possible permanent coloration was produced.

The permanganate solution employed in the analysis was standardized first against a standard solution of oxalic acid and then against a solution containing accurately known amounts of both hydrazine sulphate and oxalic acid. The procedure followed in this standardization was identical with that adopted in the analysis. By subtracting from the total volume of permanganate solution used the volume required for the complete oxidation of the oxalic acid, the volume consumed by the hydrazine present was ascertained. From these results may be calculated the value of the permanganate solution in terms either of the monoxalate or of the dioxalate. One cc. of permanganate solution employed was found to correspond to 0.00213 gram of $N_2H_4.H_2C_2O_4$.

The results of the analysis are recorded in Table I:

TABLE I.

No. of experiment.	Weight of $N_2H_4.H_2C_2O_4$	$KMnO_4$ solution used. Calculated. cc.	Found. cc.	Weight of N_2H_4 $H_2C_2O_4$ found.	Per cent N_2H_4 $H_2C_2O_4$ found
1	0.0530	24.8	24.8	0.0530	100.0
2	0.0446	20.9	20.8	0.0443	99.3
3	0.0449	21.0	21.2	0.0451	100.4
4	0.0461	21.6	21.6	0.0461	100.0
5	0.0561	26.3	26.5	0.0564	100.5
6	0.0503	23.6	23.5	0.0501	99.6
7	0.0576	27.0	27.0	0 0576	100.0

Properties.—The dioxalate of hydrazine crystallizes in glistening needles, without water of crystallization.

As compared with the monoxalate, the dioxalate of hydrazine is only sparingly soluble in water. The following procedure was followed in the to the acid solution for hydrazine with Fehling's solution yielded negative results. (*b*) The liquid condensate showed a slight alkaline reaction toward litmus and responded feebly to tests with iodate for hydrazine. On evaporation a slight residue was obtained which was identical with the white sublimate described below. Acidification caused effervescence. (*c*) The white sublimate was removed from the side arm of the distilling flask, partly in solution and partly in suspension in a small amount of water; in this solvent it was not very soluble On the evaporation of a few drops of the aqueous solution there separated out what, through the microscope, appeared to be small, amorphous particles. It was more soluble in hot water than in cold, and it also dissolved readily in dilute sulphuric acid. The solution in acid was not accompanied by any effervescence, which fact showed the absence of carbonates. Negative results were obtained from tests for cyanides and also for hydrazine by the iodate method. Ammonia was freely evolved when sodium hydroxide was added to the warm aqueous solution of the compound. When heated on the platinum plate, the substance decomposed and left a deposit of carbon, thus showing the presence of organic matter.

---

[1] Browne and Shetterly, *Loc. cit.*

(4) This experiment was designed to parallel as closely as possible the corresponding experiment on the decomposition of the monoxalate.

A sample of dried crystals, 0.5030 gram in weight, gave rise on decomposition to a total volume of gas of about 127 cc., of which 116.8 cc. were analyzed. When this volume of the gas was subjected to the action of the different absorbents there was a contraction in potassium hydroxide solution of 68.9 cc., corresponding to 59.1 per cent. of carbon dioxide and hydrocyanic acid or cyanogen; in alkaline pyrogallol, a slight contraction representing a trace of oxygen; and in ammoniacal cuprous chloride, a decrease in volume of 19.8 cc., corresponding to 17.0 per cent. of carbon monoxide. The residue, which occupied a volume of 27.5 cc., equal to 23.5 per cent. of the total volume, was assumed to be nitrogen.

(5) It was noticed in the melting point determination of the dioxalate that, when a sealed capillary tube was used, at a temperature of 200°, a liquid was formed which did not solidify on cooling. In order to study this decomposition more thoroughly the following procedure was adopted.

A small sample of the pure, dry dioxalate was sealed in a section of combustion tubing, from which the air had been exhausted by means of a mercury pump, and was heated in a bomb furnace for about one-half hour at a temperature varying from 200° to 210°. A certain volume of xylene was enclosed with the tube in the bomb so that the internal pressure exerted by the gases evolved during the decomposition might be equalized in part by the external pressure developed by the vapor of the xylene. When the tube was removed from the bomb the substance which it contained was found to be a clear, sirupy liquid.

On examination, the liquid as well as the vapor showed marked alkalinity toward red litmus. By means of suitable tests, cyanides were found to be absent; in Fehling's solution very small amounts of the liquid were sufficient to produce a decided reduction.

This liquid was allowed to stand for several days in a tube closed only with a cork whereupon a white crystalline solid separated out. The crystals were washed thoroughly with absolute alcohol, in which they showed only slight solubility The alcohol precipitated more crystals from the mother liquid. The crystalline substance was dissolved in water from which, on evaporation, it separated readily in glistening needles. It was found to reduce acidified potassium iodate and contained no carbonic or hydrocyanic acid. The addition of a few drops of calcium chloride solution to the aqueous, ammoniacal solution of the substance resulted in no precipitation whatever. The subsequent tests, made microchemically, with the same reagents but in a much more concentrated solution, resulted in a decided precipitation, appearing to indicate the presence of an oxalate. A quantitative determination of oxalic acid in a weighed sample was then attempted with the surprising result that when the supposed precipitate of calcium oxalate was being washed on the filter with hot water, it completely dissolved.

The results of this series of experiments show that the dioxalate, when subjected to destructive distillation in absence of air, breaks down with formation of water, ammonia, hydrocyanic acid, probably combined, carbon dioxide, carbon monoxide, nitrogen and carbon. An unidentified white compound of ammonia appears as a sublimate. The decomposition in a sealed tube leads to the formation of a substance which appears to be a hydrazine compound of a carboniferous acid. This unidentified acid, in concentrated aqueous solution, forms a calcium salt, insoluble in cold water but soluble in hot water.

On comparing the respective products of decomposition of the two oxalates, it is seen that intramolecular oxidation in the case of a dioxalate results in the almost complete destruction of the hydrazine radical, so that only minute amounts of that substance are found among the products, while, in that of the monoxalate, where the amount of acid present is only one-half as great, the oxidation is so incomplete that hydrazine is freely evolved. Also, where an ammonium compound, appearing as a sublimate, is formed from the dioxalate, from the monoxalate is produced a hydrazine compound. Both substances appear to be a salt of an acid containing carbon.

A comparison of the two substances obtained respectively from the destructive distillation of the monoxalate and the heating of the dioxalate in a sealed tube, neither as yet having been subjected to a quantitative analysis, indicate that they are closely related if not identical. This judgment is based on the similarity of their behavior toward certain reagents and when heated in melting-point tubes; neither exhibits a definite melting point, but the one duplicates closely the behavior of the other at like temperatures.

Titration of Hydrazine Dioxalate with Standard Alkali.—Salts of hydrazine, such as the dichloride[1] and the disulphate, show an acid reaction in aqueous solution.

One-half of the acid in the salts behaves as so much free acid[2] and may be titrated with alkalies. In agreement with the other diacid salts, hydrazine dioxalate is likewise acid in its reactions. Consequently attempts were made to titrate its free acid.

In previous titrations methyl orange has been employed, but on account of its lack of sensitiveness to oxalic[3] acid it could not be used in these experiments.

Curtius[4] has shown that the indicators—methyl orange, cochineal, corallin, tropeolin, fluorescein and litmus—give definite end points when used in the titration of hydrazine hydrate with 0.1 *N* H_2SO_4. He did not show, however, what the condition of the hydrazine at this end point was with respect to its combination with the acid. Cohn states that litmus and corallin are sensitive to oxalic acid. The titration of hydrazine dioxalate with azolitmin and with rosolic acid as indicators fail to give with any degree of sharpness the point of neutralization of that salt. Titrations with standard sulphuric acid with the extremely sensitive indicator, erythrosin, however, of a solution made alkaline by the addition of a definite volume of standard sodium hydroxide, gave results which indicated that the neutral point corresponds to the presence in the solution of only the monoxalate. The reaction may be represented by the following equation:

$$2N_2H_4.H_2C_2O_4 + 2NaOH = (N_2H_4)_2.H_2C_2O_4 + Na_2C_2O_4 + 2H_2O.$$

With phenolphthalein as indicator, the whole of the oxalic acid may be titrated with sodium hydroxide solution. In the case of none of the indicators tried was a sharp end point obtained.

CORNELL UNIVERSITY, September, 1909.

THE EXACT DETERMINATION OF SULPHUR IN SOLUBLE SULPHATES.

BY E. T. ALLEN AND JOHN JOHNSTON.

Received February 14, 1910.

It was in the course of an investigation of the sulphides of iron that our attention was first directed to the inaccuracy of the ordinary sulphur determination. Without going into the details of the analytical methods, it is finally necessary in all of them to precipitate the sulphur from a mixture of sulphate and chloride. The results we obtained were invariably low, and here surprisingly so, as the errors are magnified by the large percentage of sulphur in these compounds (53.4 per cent. in FeS_2). The ordinary methods, which, even in very careful work, easily involve a loss of 2 per cent. or more of the total sulphur, were inadequate for the purposes of our problem, and we were therefore forced to investigate them. The complications we encountered led us somewhat farther afield than we at first intended, though the importance of the analytical problem and some considerations of a more general nature seemed to justify this. Several sources of error were discovered, satisfactorily accounting, in the end, for all the losses. Some of these, it is true, have been noted by other observers, for the field is an old one, but nowhere in the literature has the subject been treated on a systematic, quantitative basis.

---

[1] Curtius and Schulz, *J. prakt. Chem.*, 42, 521 (1890).

[2] Stollé, *Ibid.*, [2] 66, 332–8 (1902).

[3] Cf. Cohn, "Indicators and Test-papers," 2nd Ed., p. 114.

[4] Curtius and Schulz, *loc. cit.*

The most important of the errors are involved in the precipitation of the sulphur after it has been transformed into soluble sulphate, and to these we will confine our attention in this paper.

Richards and Parker[1] and Hulett and Duschak[2] have studied the precipitation of *sulphuric acid* by barium chloride and of barium chloride by sulphuric acid. Their work shows that the barium sulphate thrown down under these conditions always weighs too much, because it is contaminated with barium chloride which cannot be washed out; and that exact results may be obtained by determining the chlorine in the precipitate and deducting the barium chloride equivalent to it from the weight of the crude barium sulphate. This part of the subject appears to be satisfactorily settled. The little we have done on it only confirms the statements of the authors quoted.

We have devoted nearly all of our attention to the precipitation of sulphur from *soluble sulphates*—a case which occurs much more frequently in actual practice. Here the results are always low, at least this is true of the sulphates of sodium, potassium and ammonium. We will consider first the precipitation of solutions of pure sodium sulphate.

A. The Precipitation of Sodium Sulphate by Barium Chloride.

The purity of the salt we used in our work was carefully tested in the following manner:

To free it from moisture, a thin layer of the powdered salt was heated in platinum to 200–225° for an hour or more. After the heating, we found it could be melted without losing more than 0.02 per cent. of its weight. Then it was transformed into sodium chloride by the addition of a slight excess of barium chloride; the barium sulphate was filtered out and the soluble chloride in the filtrate evaporated to dryness, heated to incipient redness, and weighed. To this quantity was added a correction for a certain amount of sodium, calculated to chloride, which was carried down by the precipitate.[1]

---

[1] *Proc. Am. Acad.*, 31, 67 (1896); *Z. anorg. Chem.*, 8, 413 (1895).

[2] *Z. anorg. Chem.*, 40, 196 (1904).

(*a*) 1.2160 g. Na_2SO_4 gave 1.0026 g. NaCl. Calculated, 1.0008 g.
(*b*) 1.2156 g. Na_2SO_4 gave 1.0009 g. NaCl. Calculated, 1.0003 g.

Potassium was sought for by treating the total chlorides (from another portion of salt) with an equivalent quantity of chloroplatinic acid and evaporating to dryness on the steam bath. The residue was treated with successive portions of 93 per cent. alcohol till the greater part was dissolved, when the remainder was dried, a little more platinum solution added, and the procedure repeated. A little characteristic golden yellow residue was obtained.

(*a*) 0.995 g. chlorides gave 2.9 mg. K_2PtCl_6, equivalent to 0.08 per cent. K_2SO_4 in the original salt.

(*b*) 0.997 g. chlorides gave 3.3 mg. K_2PtCl_6, equivalent to 0.09 per cent. K_2SO_4.

The precipitated barium sulphate was also examined for potassium, but none was found in it. This quantity of another sulphate is, of course, too small to make any appreciable difference in the weight of our barium sulphate precipitates. The only other impurity noted in the sodium sulphate was a trace of iron.

Method of Precipitation.—The sulphate, dried as previously described, was, in some cases, weighed directly, but in general, to avoid exposing the anhydrous substance frequently to the air, a given quantity of salt was made up to a given weight of solution and weighed portions of this were taken for individual determinations.

About 24.35 grams dried sodium sulphate, weighed carefully to the milligram, was put into a tared flask and diluted till the solution weighed about 1000 grams. The weight was determined to the nearest centigram. Portions of this solution of about 50 grams were then weighed to the milligram in a weight burette, making all necessary corrections for the buoyancy of the air. This was then diluted in a Jena glass beaker to 350 cc. with hot water, acidified with a measured quantity of hydrochloric acid, heated to boiling, and precipitated by a slight excess of 10 per cent. solution of barium chloride (*i. e.*, a solution containing 100 grams $BaCl_2.2H_2O$ in 1 l.). Two grams $BaSO_4$ requires 20.9 cc. 10 per cent. $BaCl_2$ solution; while we used 22–22.5 cc.[2] The reagent was let into the sulphate solution from a burette, either drop by drop, or, better, in a thin stream which flowed down the side of the beaker.

---

[1] The method of this correction will be described later (page 594).

[2] A greater excess was shown to exert no appreciable influence on the results (see p. 597).

The precipitates were commonly allowed to stand for about 18 hours, filtered on paper, and thoroughly washed till the filtrate showed only the merest opalescence with silver nitrate;[1] this required 1 to $1^1/_2$ hours' washing with precipitates of 2 grams. The moist precipitate and filter are then burned *very slowly and carefully* in a platinum crucible. The filter must not be allowed to take fire, for in spite of some statements to the contrary, we find the sulphate is readily reduced and not easy to oxidize completely, once reduction has taken place—at least this is true of large precipitates. As soon as the filter is entirely burned, the crucible cover is moved to one side to admit the air, the temperature raised and the heating continued till the weight is constant. Once the paper is burned, a further heating of 20 minutes will very nearly suffice.

Gooch crucibles were also tried They obviate all danger of reduction, of course, and are well adapted to small precipitates; but large precipitates are inclined to clog the filter and demand much time in washing. For this reason the results are likely to be somewhat high when Gooch crucibles are used.

The precipitates prepared as described weighed about 2 grams each. We chose this quantity for two reasons: first, it is about the quantity of barium sulphate yielded by 0.5 gram of iron pyrites; and second, and more important, it is a quantity sufficiently large to trace the small percentage errors with some degree of certainty.

Determinations of the sulphur in pure sodium sulphate carried out in this manner are always too low, the deficit varying with the conditions from 0.3 per cent. to 0.5 per cent., and sometimes even more. We will now take up these errors in order.

1. Loss Due to "Solubility."[2]—This is the most obvious source of error, and though the least important, unless the precipitate is quite small, it is much increased by free acid. We have determined it in the usual way by evaporating the filtrate and washings to dryness in a platinum basin, adding a little water to the residue, and filtering on a very small ashless paper. Great pains were taken to remove any adhering film from the dish, to avoid loss of any material by running through the filter, and to wash the precipitate completely. Table I shows the losses from solubility. It will be noted that these increase with the concentration of acid in the original solution, and therefore that the less acid one chooses, the better, so far as this loss is concerned. Later, it will apof a slight excess of barium chloride; the barium sulphate was filtered out and the soluble chloride in the filtrate evaporated to dryness, heated to incipient redness, and weighed. To this quantity was added a correction for a certain amount of sodium, calculated to chloride, which was carried down by the precipitate.[1]

---

[1] A test with a very dilute standard solution showed the chlorine at this stage to be equal to about 0.005 mg. in 25 cc. of the washings.

[2] These losses are not in every case to be referred entirely to the solubility of barium sulphate in the supernatant liquid; but may be in some cases partly due to the well-known tendency of barium sulphate to creep. Hence the figures given in the table are to be taken, not as quantitative measurements of this solubility, but as analytical corrections.

(*a*) 1.2160 g. Na_2SO_4 gave 1.0026 g. NaCl. Calculated, 1.0008 g.
(*b*) 1.2156 g. Na_2SO_4 gave 1.0009 g. NaCl. Calculated, 1.0003 g.

Potassium was sought for by treating the total chlorides (from another portion of salt) with an equivalent quantity of chloroplatinic acid and evaporating to dryness on the steam bath. The residue was treated with successive portions of 93 per cent. alcohol till the greater part was dissolved, when the remainder was dried, a little more platinum solution added, and the procedure repeated. A little characteristic golden yellow residue was obtained.

(*a*) 0.995 g. chlorides gave 2.9 mg. K_2PtCl_6, equivalent to 0.08 per cent. K_2SO_4 in the original salt.

(*b*) 0.997 g. chlorides gave 3.3 mg. K_2PtCl_6, equivalent to 0.09 per cent. K_2SO_4.

The precipitated barium sulphate was also examined for potassium, but none was found in it. This quantity of another sulphate is, of course, too small to make any appreciable difference in the weight of our barium sulphate precipitates. The only other impurity noted in the sodium sulphate was a trace of iron.

Method of Precipitation.—The sulphate, dried as previously described, was, in some cases, weighed directly, but in general, to avoid exposing the anhydrous substance frequently to the air, a given quantity of salt was made up to a given weight of solution and weighed portions of this were taken for individual determinations.

About 24.35 grams dried sodium sulphate, weighed carefully to the milligram, was put into a tared flask and diluted till the solution weighed about 1000 grams. The weight was determined to the nearest centigram. Portions of this solution of about 50 grams were then weighed to the milligram in a weight burette, making all necessary corrections for the buoyancy of the air. This was then diluted in a Jena glass beaker to 350 cc. with hot water, acidified with a measured quantity of hydrochloric acid, heated to boiling, and precipitated by a slight excess of 10 per cent. solution of barium chloride (*i. e.*, a solution containing 100 grams $BaCl_2.2H_2O$ in 1 l.). Two grams $BaSO_4$ requires 20.9 cc. 10 per cent. $BaCl_2$ solution; while we used 22–22.5 cc.[2] The reagent was let into the sulphate solution from a burette, either drop by drop, or, better, in a thin stream which flowed down the side of the beaker.

---

[1] The method of this correction will be described later (page 594).

[2] A greater excess was shown to exert no appreciable influence on the results (see p. 597).

The precipitates were commonly allowed to stand for about 18 hours, filtered on paper, and thoroughly washed till the filtrate showed only the merest opalescence with silver nitrate;[1] this required 1 to $1^1/_2$ hours' washing with precipitates of 2 grams. The moist precipitate and filter are then burned *very slowly and carefully* in a platinum crucible. The filter must not be allowed to take fire, for in spite of some statements to the contrary, we find the sulphate is readily reduced and not easy to oxidize completely, once reduction has taken place—at least this is true of large precipitates. As soon as the filter is entirely burned, the crucible cover is moved to one side to admit the air, the temperature raised and the heating continued till the weight is constant. Once the paper is burned, a further heating of 20 minutes will very nearly suffice.

Gooch crucibles were also tried. They obviate all danger of reduction, of course, and are well adapted to small precipitates; but large precipitates are inclined to clog the filter and demand much time in washing. For this reason the results are likely to be somewhat high when Gooch crucibles are used.

The precipitates prepared as described weighed about 2 grams each. We chose this quantity for two reasons: first, it is about the quantity of barium sulphate yielded by 0.5 gram of iron pyrites; and second, and more important, it is a quantity sufficiently large to trace the small percentage errors with some degree of certainty.

Determinations of the sulphur in pure sodium sulphate carried out in this manner are always too low, the deficit varying with the conditions from 0.3 per cent. to 0.5 per cent., and sometimes even more. We will now take up these errors in order.

1. Loss Due to "Solubility."[2]—This is the most obvious source of error, and though the least important, unless the precipitate is quite small, it is much increased by free acid. We have determined it in the usual way by evaporating the filtrate and washings to dryness in a platinum basin, adding a little water to the residue, and filtering on a very small ashless paper. Great pains were taken to remove any adhering film from the dish, to avoid loss of any material by running through the filter, and to wash the precipitate completely. Table I shows the losses from solubility. It will be noted that these increase with the concentration of acid in the original solution, and therefore that the less acid one chooses, the better, so far as this loss is concerned. Later, it will ap-

---

[1] A test with a very dilute standard solution showed the chlorine at this stage to be equal to about 0.005 mg. in 25 cc. of the washings.

[2] These losses are not in every case to be referred entirely to the solubility of barium sulphate in the supernatant liquid; but may be in some cases partly due to the well-known tendency of barium sulphate to creep. Hence the figures given in the table are to be taken, not as quantitative measurements of this solubility, but as analytical corrections.

TABLE I.—LOSSES (IN MG.) DUE TO THE SOLUBILITY OF $BaSO_4$.
Total volume = 350 cc. + 350 cc. washings.

cc. 20 per cent. HCl.						Mean.
0.2	—1.3	1.0	0.9	0.6	0.7	0.9
1.0	—1.6	1.4	.	.	. .	1.5
5.0	3.5	3.1	.	.	. .	3.3
10.0	4.1	3.7	.	.	.	3.9
20 0	14.3	10.0	.	...	.	12.0
100.0	36.5	....	.	. .		36.0

pear that another and more important error is influenced by the same cause. In most of our work we have used one of two acid concentrations, *viz.*, 2 cc. of 2 per cent.[1] or 1 cc. 20 per cent. hydrochloric acid, the volume of the solution being 350 cc. The stronger acid has the advantage that the precipitates formed in its presence are somewhat denser and more convenient to handle, but the weaker acid is to be recommended, since the sum of the corrections in that case is smaller. The quantity of free acid *ordinarily* used in the sulphate determination is doubtless too great, and may cause large percentage errors on precipitates which weigh only a few hundred milligrams.[2]

The statement has been made by several chemists that alkaline chlorides greatly increase the solubility of barium sulphate.[3] Determinations of the solubility by the above method in solutions containing 10 grams sodium chloride in 350 cc. showed that the chloride was practically without influence. As these results were perfectly consistent with the rest of our work on sodium sulphate, nothing more was done on the question, but as regards the solvent effect of potassium and ammonium chlorides which is commonly held to be greater, we have definitely disproved that in another way (see Tables XX and XXV).

2. *The Occlusion*[4] *of Sodium Sulphate by Barium Sulphate.*—Table II gives a number of determinations of barium sulphate from a weighed quantity of sodium sulphate, and the corresponding deficits. It will

TABLE II.—TOTAL LOSSES (IN MG.) IN THE PRECIPITATION OF PURE SODIUM SULPHATE.

cc 20 per cent HCl in the solution	0 2.					1 0			
$BaSO_4$ calc	2002.2	1995.4	2044.5	2039.9	2036 6	2002 6	2037.4	1998.0	1994.5
$BaSO_4$ found .	1994 7	1985.5	2032.6	2035.7	2029.4	1995.5	2030.3	1985.7	1987.4
Deficit in mg.	7 5	9.9	11.9	4.2	7.2	7.1	7.1	12.3	7.1

---

[1] For convenience, both will be stated in terms of 20 per cent. acid.

[2] Thus Folin (*J. Biochem.*, 1, 147 (1906)) prescribes as safe limits of acidity 1–4 cc conc hydrochloric acid in 150 cc. solution, *i. e.*, 4.5 cc. -18.5 cc. 20 per cent. acid in 350 cc.

[3] R. Fresenius and E. Hintz, *Z. anal. Chem.*, 35, 75 (1896); Lunge and Stierlin, *Z. angew. Chem.*, 18, 1929 (1905); Folin, *J. Biochem.*, 1, 142 and 144 (1906).

[4] By occlusion we mean, simply, retention by the precipitate without implying its nature.

be seen at once that the solubility correction (Table I) accounts for only a small part of the total loss.

In the sixth German edition of his "Quantitative Analysis" (Vol. I, p. 230, (1875)), Fresenius says that, when barium is precipitated by sulphuric acid in the presence of alkalies, small portions of alkali sulphates are carried down with the precipitate, but he gives no data. Hintz and Weber[1] found that, when barium sulphate, which had been precipitated from an ammonium sulphate solution, was heated in a glass tube, a sublimate containing sulphate was obtained. Lunge and Stierlin[2] give results of four determinations of sodium and potassium sulphates in crude barium sulphate, by digesting the latter with dilute hydrochloric acid. No evidence as to the completeness of the separation is offered.[3] We examined the weighed precipitate for impurities as follows:

The precipitate was dissolved in about 15 cc. pure conc. sulphuric acid in a platinum dish. The solution was cooled and poured in a thin stream into about 350 cc. water with vigorous stirring. The solution and precipitate were heated to facilitate filtering, after which the solution was evaporated over a free flame till fumes of sulphuric acid appeared, and then carried to dryness in a hood with good draft. The residue in the platinum basin was now dissolved in a little water and filtered through a 5.5 cm. filter into a small tared platinum dish. The contents were evaporated to dryness on the steam bath, then heated carefully to redness, cooled and weighed. The white soluble salt obtained could hardly be anything but sodium sulphate, nevertheless one of the residues was converted into barium sulphate and the point proved. 0 0234 gram residue gave 0 0386 gram $BaSO_4$; calc. for Na_2SO_4, 0 0385 gram. In order to find whether all the sodium sulphate is recovered from the precipitate by the above method, the precipitate obtained by pouring the sulphuric acid solution into water was dried, ignited, and again dissolved in sulphuric acid and reprecipitated by water. The results of four such experiments follow:

Na_2SO_4 (in mg.) from first extraction	10.1	11.8	24.8	26.2
Na_2SO_4 (in mg.) from second extraction	0.8	1.3	2.1	2.0

The second extraction recovers so nearly 10 per cent. of the amount obtained by the first extraction that in all subsequent data the amount *actually obtained* by one extraction will be given, but the correction will be made on a quantity 10 per cent. greater. This probably is as accurate as a direct determination would be.

Table III shows the amount of sodium sulphate found in precipitates formed under the conditions stated above, and also the corresponding corrections. Since all the sodium sulphate in the precipitate should, of course, have been converted into barium sulphate, the precipitate weighs too little. The numbers designated "correction" in the table are obtained by multiplying the weight of the occluded sodium sulphate, plus 10 per cent., by the factor $91.37/142.07 = (BaSO_4 - Na_2SO_4)/Na_2SO_4$.

---

[1] *Z. anal. Chem.*, 45, 39 (1906).

[2] *Z. angew. Chem.*, 18, 1921 (1905).

[3] We later discovered that water alone will extract from an *ignited* precipitate about 80 per cent. of the alkali salt.

TABLE III.—OCCLUSION OF SODIUM SULPHATE BY BARIUM SULPHATE.
Na_2SO_4 (in mg.) occluded by 2 grams precipitate[1] with the corrections.

0.2 cc. 20 per cent. HCl..	8.7	7.1	9.1	5.3	8.3	4.7	11.9	11.6
Corrections.............	6.1	5.0	6.4	3.7	5.8	3.3	8.3	8.1
1.0 cc. 20 per cent. HCl..	11.6	8.4	11.4	12.0	10.3	7.1	7.7	9.4
Corrections.............	8.1	5.9	8.0	8.4	7.2	5.0	5.4	6.5

This sodium sulphate is originally present as such in the barium sulphate. It is not present in the form of sodium chloride, as one might suspect. At least, this is true of the *ignited* precipitates. We have repeatedly tested our precipitates for chlorine by the quick and accurate method of Hulett and Duschak.[2] This consists in dissolving the precipitate in sulphuric acid, in a simple apparatus of glass swept by a current of air which carries the free hydrochloric acid into a solution of silver nitrate. We heated directly with a small flame, instead of a hot water bath, as Hulett and Duschak did, thereby dissolving the precipitate in a much shorter time, though now and then a determination is lost by the cracking of the tube. The silver chloride was determined gravimetrically instead of volumetrically, which was more convenient and sufficiently accurate for our purpose.

Precipitates prepared and washed as we have directed in the foregoing never gave more than 0.5 mg. of chlorine *after ignition*, and we have repeatedly reduced the quantity to 0.1 mg., even when the original solution contained 15 to 30 grams sodium, potassium, or ammonium chloride per liter. This is shown in Table IV. We will later show that the washed, but unignited, precipitates contain usually 1–2 mg. of chlorine, which is probably present as barium chloride; this is considerably increased when the precipitate is rapidly formed. The chlorine is practically all lost on ignition, if the precipitate has been slowly formed.

TABLE IV.—CHLORINE (IN MG.) IN 2 GRAMS IGNITED PRECIPITATE.
From Na_2SO_4 solutions containing HCl as below; V = 350 cc.

	cc. 20 per cent. HCl in soln.						
Grams NaCl.	1 drop	0.1	0.2	1.0	5.0	20.0	100.0
0	1.0	0.2	0.4	0.2 and 0.4	0.1	0.6	4.0
4	...	...	...	0.1	...	...	...

---

[1] Volume of original solution = 350 cc.

[2] *Loc. cit.*, p. 197.

The next step in the investigation was naturally to study the causes which condition the occlusion of sodium sulphate by the precipitate.

Influence of Various Factors on the Composition of the Precipitate.

(*1*) *The Effect of Concentration of the Sodium Sulphate.*—Table V gives a comparison of the quantities of sodium sulphate found in 2 grams barium sulphate precipitated from sodium sulphate solutions of several concentrations, the other conditions remaining the same. It will be seen that increasing the volume from 350 to 2000 cc. reduces the quantity slightly. The last two experiments are instructive. Equivalent solutions of barium chloride and sodium sulphate, each 100 cc. in volume and of such a concentration as to give about 2 grams of barium sulphate, were allowed to drop slowly and at the same rate (100 cc. in about 4 hours) into 8 liters of cold water, which was vigorously stirred during the whole process. The conditions in the two experiments differed only in the amount of acid in the solution. The quantity of sodium sulphate occluded, instead of being reduced by this high dilution, was a trifle increased thereby, though possibly this increase may be due to the fact that these precipitates were thrown down in the cold. It is evident from this that dilution alone is of little influence in reducing occlusion of sodium sulphate.

TABLE V.—EFFECT OF CONCENTRATION OF SODIUM SULPHATE.

Quantities of sodium sulphate occluded by 2 grams precipitate.

Volume in cc.	cc. 20 per cent. HCl	Mg.						
350	1	11.6	8.4	11.4	12.0	10.3	.	...
1000	5	6.0	8.9	. .		..	.	. .
2000	10	8.0	6.9	6.9	8.2	8.9	6.4	5.3
8000	5	10.9	[precipitated cold]					
8000	25	9.6	[precipitated cold]					

(*2*) *Effect of the Rate of Addition of the Reagent.*—The rate at which the solution is precipitated has some influence on occlusion, though it is not very great. Thus, if the reagent is allowed to flow as rapidly as possible from the burette (time = 9 seconds in the burette we used), the quantity of sodium sulphate taken up by the precipitate is reduced somewhat, though the results here are not so uniform as they are when the rate is slower (see p. 603).

(*3*) *The Effect of Pouring the Sulphate into the Barium Chloride.*—The few results obtained in this way indicate that no effect is to be attributed to this cause. In the three following experiments the barium chloride solution was diluted to 350 cc., acidified, and heated to boiling. Then the sulphate solution in 50 cc. volume was poured as slowly as possible into it with constant stirring. In three different experiments, the quantities of sodium sulphate occluded in 2 grams precipitate were 11.6 mg., 8.4 mg., and 12 mg.

(4) *The Effect of Acid Concentration.*—The concentration of the hydrochloric acid in the sulphate solution was found to reduce the occluded alkali sulphate very slowly, as may be seen from Table VI, but free acid increases the other errors more than it diminishes this one.

TABLE VI.—EFFECT OF ACID CONCENTRATION ON OCCLUSION.

Na_2SO_4 (in mg.) in 2 grams precipitate. V = 350 cc.

cc. 20 per cent. HCl.	0.2.	1.	5.	10	20.	100.
..	8.7	7.1	7.7	4.1	3.6	2.5
..	9.1	7.7	..	5.1	..	.
...	7.1	9.4	..	..	.	..

(5) *Influence of Time.*—There is a noticeable change in the composition of the precipitate if it is left to stand in the supernatant liquid. A precipitate which is filtered and washed immediately after precipitation always contains more sulphate than one which has been left to stand, and the difference is considerable when the initial quantity of occluded sodium sulphate is large.

TABLE VII.—EFFECT OF THE TIME OF STANDING ON OCCLUSION.

Mg. sodium sulphate in 2 grams precipitate.

Time. Hours.	Vol. cc.	NaCl. Gms	cc 20 per cent. HCl						
1/4	350	0	0 2	11.9	11.6	...	..		..
1/4	350	5	0.2	22.6	22.7		.		...
3	350	5	0 2	18.3	19.0	18.5	19.7	18.4	19.7
3	2000	0	1.0	6.9	6 9	8.2	8.9	.	
18	350	0	0.2	8.7	9.1		.		
18	350	5	0.2	17.3	17 1	17.5	17.2	17.9	....
18	2000	0	1.0	8.0	5 3	6.4	.	.	. .
45	350	0	0.2	5.3		.	..	..	...
45	350	5	0.2	14.0	14.2	.	...	...	....
70	350	5	0.2	12.6	11 9	...	....	..	....

(6) *Effect of Digesting the Precipitate.*—In order to test this point, a number of precipitations were made in the usual way from solutions of sodium sulphate containing 5 grams sodium chloride and 0 2 cc. 20 per cent. hydrochloric acid. Of these precipitates two were allowed to stand in contact with the original supernatant liquid for three hours on the steam bath; the precipitate was then filtered off, and the occluded sodium sulphate, determined in the usual way, was (1) 18.3 mg., and (2) 19.0 mg. In the other four cases, the supernatant liquid was poured off immediately after the precipitation and the precipitate was treated as follows, the time of contact with the liquid being in each case three hours on the steam bath.

	Amount of Na_2SO_4 in mg.
(3) Filtered and washed ppt. until free from Cl.; added 350 cc. hot water.	18.4
(4) Added 350 cc. hot water..............................	19.7
(5) Added 350 cc. hot water containing 1.2 grams Na_2SO_4....	18.5
(6) Added 350 cc. hot water containing 1.0 gram $BaCl_2$..............	19.7

From these results it is evident that the amount of sodium sulphate still occluded by the precipitate at the end of three hours on the steam bath, is independent of the composition and concentration of the supernatant liquid. The explanation of these results appears to be that the impurities in the precipitate react chemically with one another, forming barium sulphate and sodium chloride, and that it is the latter—not sodium sulphate—which diffuses out into the supernatant liquid (see paragraph 5). At any rate, it is evident that in an analysis nothing is gained by digesting the precipitate with a large excess of reagent.

(7) *Influence of Concentration of Sodium Chloride.*—It has been shown that a considerable variation in the concentration of a sodium sulphate solution exerts only a small influence on the content of the same in the barium sulphate precipitated from it. When the concentration of the sodium is increased by adding *sodium chloride* to the original solution, the occlusion of sodium sulphate is markedly increased. In Table VIII this influence is brought out. It appears that a concentration of sodium chloride of about 30 grams per liter causes an error of about 0.75 per cent. of the total sulphur from this source alone. The importance of this error is evident when it is remembered that alkali chlorides are commonly present in considerable quantity in solutions which have to be analyzed for sulphur. The effect of concentrations of chlorides greater than the above were not studied. Again, it should be stated that the presence of sodium chloride does not occasion the occlusion of the chloride as such. The ignited precipitates contain only a minute trace of chloride. Later we found that precipitates before ignition contained a small quantity, but the evidence goes to show that it is present as barium chloride, and that it is partly eliminated as hydrochloric acid during ignition.

TABLE VIII.—EFFECT OF SODIUM CHLORIDE ON THE OCCLUSION OF SODIUM SULPHATE.

Mg sodium sulphate in 2 grams precipitate

NaCl Grams	cc. 20 per cent HCl	Time Hours		
0	0.2	18	8.3	(Average from Table III)
0	1.0	18	8.0	(Average from Table III)
0	5.0	18	7.7	
2	0.2	1/2	14.0	
2	5.0	1/4	10.0	
5	0.2	18	17.4	(Average from Table III)
5	5.0	1/4	16.4	
5	5.0	18	11.5	
10	0.2	1/4	24.8	26.2
10	0.2	18	17.8	
10	1.0	18	23.6	

The Volatilization of Sulphuric Acid when Precipitates Are Heated.

In many instances the losses due to solubility and the occlusion of sodium sulphate, together, make up nearly the whole deficit in sulphate determinations, but in others, *e. g.*, where the quantity of acid or of sodium chloride is considerable, the loss still unaccounted for may be equal to the sum of the above-named errors. As we could conceive of no other possibility, we tried experiments to find if the precipitates lost anything when they were heated.

To this end precipitates prepared and washed as usual were dried (in a toluene bath) at 105°. They were then carefully detached from the paper by tapping, and put into a tubulated platinum crucible (Gooch's) adapted to the determination of any volatile product.[1] The joint between cover and crucible was sealed with sodium tungstate, and the outlet tube was connected with a Liebig potash bulb which contained 10 cc. water and 1 cc. Merck's perhydrol free from sulphur. A current of pure dry air was drawn through the apparatus while the crucible was heated strongly by means of a Bunsen burner, the outlet tube from time to time being also heated with the free flame to drive out the volatile products. The contents of the bulb proved to contain sulphuric acid when tested in the usual way. A large number of subsequent experiments showed that barium sulphate precipitates thrown down from acidified sodium sulphate solutions, *always* lose sulphuric acid when they are ignited in this way. The tubulated crucible was used for all the earlier determinations given in this paper. For the greater losses caused by the chlorides of potassium and ammonium, it gave, for some reason, results entirely too low. A platinum combustion tube[2] and boat were therefore substituted. The tube must be heated with a blast, otherwise the barium sulphate in the boat does not reach a temperature comparable with that in an ordinary sulphur determination. In cases where the loss is large, two bulbs are required for complete absorption. Perhydrol must be used in the bulbs, otherwise there is a partial loss of sulphur dioxide which is formed by the dissociation of the sulphuric acid. Blanks were tried at various times but no trace of sulphuric acid was ever obtained from any of them. At first it was suspected that the volatilized sulphur came from a decomposition of the barium sulphate. This was disproved by the fact that the precipitates soon reach a constant weight, a point which is further supported by the work of Mostowitsch,[3] who found that barium sulphate does not appreciably dissociate under 1400°. The possibility of a reduction of the sulphate to sulphide, either by fibers of filter paper or by the hydrogen of the flame passing through the hot platinum, and a decomposition of the sulphide by moisture at the same time, was also considered. The flame surely had nothing to do with the case, because the results were the same when the crucible was heated by a resistance furnace to a temperature of about 1000°. Numerous tests on precipitates which had been heated in either way proved that they were not alkaline after ignition. These tests were very carefully conducted with hot boiled water and a drop of phenolphthalein. The solution never changed color; isolated grains sometimes turned pink, but a drop of 0.01 *N* acid was sufficient to dispel the color. This sets at rest any question of the decomposition of barium sulphate. Finally, it was shown that the quantity of sulphuric acid lost by volatilization varies greatly according to the conditions under which the precipitate was formed, but keeps pace with the deficits found on precipitates prepared under parallel conditions. Experiments showed that nearly all the loss occurs above 500°, but to heat the precipitates to this temperature would not remedy the difficulty; firstly, because water is retained by the precipitate at that temperature, and secondly, because the real difficulty is the failure to convert the sulphuric acid into barium sulphate during precipitation.

---

[1] See W. F. Hillebrand, *Bulls. U. S. Geol. Surv.*, Nos. 305 and 422, where the apparatus is described and applied to the determination of water in minerals.

[2] The authors wish to acknowledge their indebtedness to Mr. P. H. Walker, of the Bureau of Chemistry, for the loan of the combustion tube.

[3] *Metallurgie*, 6, 450 (1909).

Influence of Various Factors on the Loss by Volatilization.

In general, these factors are the same as those which condition occlusion; but the degree of their influence is different.

(*1*) *Effect of Acid Concentration.*—Table IX shows how this loss varies with the concentration of hydrochloric acid in the solution from which the barium sulphate is thrown down. The loss is given in terms of barium sulphate, since the sulphuric acid volatilized should have been converted into barium sulphate during precipitation. It will be noted that the loss increases with the strength of acid up to 5 cc. of 20 per cent. hydrochloric acid in 350 cc., and then falls again. As said before, nearly all our work has been done with 0.2 cc. and 1.0 cc. of 20 per cent. hydrochloric acid in a total volume of 350 cc. (lines 2 and 3). Here the loss seems nearly proportional to the acid concentration, which again is a reason for using the smaller quantity of acid. If the sulphate is poured into the barium chloride instead of *vice versa*, the volatilization losses are reduced. Two different precipitates, of about 2 grams each, formed in

TABLE IX – SULPHURIC ACID (IN TERMS OF BARIUM SULPHATE) LOST BY 2 GRAMS PRECIPITATE.

Precipitation from Pure Sodium Sulphate; V = 350 cc.

cc. 20 per cent. HCl.	Mg. $BaSO_4$.									Mean Mg.
0.1	0.5	0.3	...	...	...	...	...	...	...	0.4
0.2	0.4	0.6	...	...	...	...	...	...	. .	0.5
1.0	2.4	1.8	2.0	2.6[1]	2.7	1.6	2.4[1]	2.1	2.7	2.2
5.0	5.4	6.4[1]	3.8[1]	4.3	3.8	4.8[1]	5.1	4.5[1]	. .	4.7
10.0	3.1	2.9	3.4[1]	2.6[1]	2.8[1]	3.1	...	...	...	2.9
20.0	1.8	2.4	1.7	1.3	1.7	. .	.	. .	.	1.8

---

[1] The figures marked [1] were derived by doubling the results obtained on 1 gram.

this way, in solutions containing 1 cc. 20 per cent. hydrochloric acid, lost sulphuric acid which yielded 0.3 mg. and 0.8 mg. barium sulphate, respectively. The quantities marked 1 in the table were derived by doubling the results obtained from 1 gram of precipitate, thus showing that the losses are proportional to the weight.

(2) *Effect of Sodium Chloride.*—Table X shows that when barium sulphate is precipitated from solutions containing sodium chloride, the acid remaining constant, the loss by volatilization is greatly increased. As chlorides are usually present where sulphates are to be determined, the importance of this fact will be instantly recognized.

(3) *Influence of Time.*—The data on this point show higher losses when precipitates are filtered and washed immediately after precipitation, and a gradual reduction of the losses when the precipitates are allowed to stand in contact with the supernatant liquid. A few data on this point are given in Table X. Where accuracy in the determination of sulphur is required, it is therefore evident that there is a real gain in allowing the precipitate to stand. We have shown that the errors, both from occlusion of sodium sulphate and from volatilization, are in this direction and the same must be true of "solubility," if there is any difference at all.

TABLE X.—EFFECT OF NaCl ON VOLATILIZATION LOSS.

H_2SO_4 (in mg. $BaSO_4$) lost by 2 grams precipitate.

Grams. NaCl	0.2 cc. 20 per cent. HCl.		1.0 cc. 20 per cent. HCl.			5.0 cc 20 per cent. HCl.	
0	0.5[1]	...	2.2[1]	...	....	4.7[1]	
2	1.7	3.4[2]	4.6	..		.	6.6[2]
5	5.4	5.3[3]	10.0	.	.	11.9	.
..	5.1	5.1	8.8		.	10.1	.
10	8.8	.	13.7	11.9	14.1[2]	...	
..	7.1	.	11.6	12.0	6.8[4]	..	..
.	...	...	..	..	12.9	..	..

(4) *Effect of Rate of Addition of the Reagent.*—We have stated previously that the rate at which the reagent is added to the solution makes little difference in the quantity of alkali sulphate retained by the precipitate. The loss by volatility, however, is markedly lowered by increasing the rate (Table XI).

The Composition of Rapidly Formed Precipitates.

The direct and natural inference from the results in this table is that rapid precipitation reduces the amount of "free" acid in the precipitate. A closer study proved this to be true. Rapid precipitation has also another effect, *viz.*, to increase the quantity of chlorine in the precipitate.

---

[1] Averages from Table IX.

[2] Filtered immediately after precipitation.

[3] Stood 3 hours on the steam bath.

[4] Stood 70 hours in the cold. All others stood 18 hours.

TABLE XI.—EFFECT OF RATE OF PRECIPITATION ON VOLATILIZATION LOSS.

H_2SO_4 (in mg. $BaSO_4$) lost by 2 grams precipitate.

Grams NaCl.	0.2 cc. 20 per cent. HCl. Time of precipitation		1 cc. 20 per cent HCl. Time of precipitation.		5 cc. 20 per cent HCl. Time of precipitation.	
	3-6 min.[1]	9 sec.	3-6 min.[1]	9 sec.	3-6 min[1]	9 sec.
0	0.5	0.4	2.2	...	4.7	0.4
5	5.2	0.6	..	..	.	..
..	.	0.7	.	.		.
10	..	..	12.4	3.7	...	.
..	..	...		4.6	...	.

Indeed, all *unignited* barium sulphate precipitates contain chlorine, however carefully they are washed. Four solutions of identical composition, *viz.*, 1.21 grams Na_2SO_4 + 5 grams NaCl + 0.2 cc. 20 per cent. hydrochloric acid in 350 cc., were precipitated in pairs, two slowly and two rapidly. The time for each of the first pair was 3–6 minutes, for the second pair 9 seconds. After the usual washing, these precipitates were dried at 105°. The chlorine was determined by Hulett and Duschak's method. 6.3 mg. and 7.2 mg., respectively, of silver chloride were obtained from the first pair, the 17.8 mg. and 20.9 mg. from the second pair. We have previously seen that the total sodium is slightly diminished by a rapid precipitation, which could not be the case were the chlorine taken up in the form of sodium chloride. Now, since barium sulphate, which is precipitated from *sulphuric acid*, also contains chlorine which Hulett and Duschak have shown to be likewise increased by rapid precipitation, and which in their case must be in the form of barium chloride, we conclude that the chlorine in all the precipitates is in the same form.

Since both "free" sulphuric acid and barium chloride exist together in the same precipitate, it is not surprising to find that during ignition some hydrochloric acid is always volatilized, formed, of course, by the chemical reaction of the two substances. We at first supposed that by this means the rapidly formed precipitates, containing as they do more chloride, reduced the volatilization of sulphuric acid. But experiment showed that the amount of hydrochloric acid thus formed is about the same, whether the precipitate had been formed slowly or rapidly; consequently the washed precipitate must contain *less* "free" sulphuric acid in the latter case. A slowly formed precipitate loses, in this way, practically all its chlorine, but a rapidly formed precipitate still contains a considerable amount. Two such precipitates formed in solutions containing 5 grams NaCl + 0.2 cc. 20 per cent. hydrochloric acid in 350 cc. retained 10.3 mg. and 10.8 mg. chlorine (in terms of silver chloride).[2] In spite of this fact, we may still lose several milligrams of sulphuric acid (in terms of barium sulphate) on heating. After ignition one may extract from such a precipitate both sodium chloride and sodium sulphate, though not the total quantity of the sodium (Table XII).

---

[1] The values given for slow precipitation are average values from Tables IX and X.

[2] Our precipitates are thus, at least partially, analogous in composition to Hulett and Duschak's, though apparently the amount of sulphuric acid their precipitates absorb, if any, is always less.

TABLE XII.—WATER EXTRACT (IN MG.) FROM IGNITED PRECIPITATES.

Precipitation from Na_2SO_4 + 5 grams NaCl + 0.2 cc. 20 per cent. HCl; V = 350 cc.

	Water extract.			Na_2SO_4 left in precipitate after extraction by water.[1]	Total sodium, calc. as Na_2SO_4.[2]
	Total.	NaCl.	Na_2SO_4.		
Precipitated in 9 sec..........	8.6	7.1	1.5	2.0	12.1
Precipitated in 9 sec..... ...	8.8	6.0	2.8	2.0	12.1
Precipitated by pouring Na_2SO_4 into $BaCl_2$ in 10 sec	8.6 11.8	4.5 2.5	4.1 9.3	4.0 3.3	13.6 15.1
Precipitated in about 3 min...	14.5	trace	14.5	..	14.5
Precipitated in about 3 min .	16.2	trace	16.2	...	16.2

We have treated the subject of rapid precipitation so much in detail because it has been advocated as the essential condition of an analytical method for the determination of sulphur by Hintz and Weber.[3] From the preceding it will now be understood that the losses by volatilization of sulphuric acid and occlusion of sodium sulphate are in the first place reduced by reason of a more complete conversion of the original sulphate into barium sulphate, and in the second place, partially compensated by an absorption of barium chloride by the precipitate. Our own results, obtained by rapid precipitation, which are given in Table XIII, prove it

TABLE XIII.—RESULTS FROM RAPID PRECIPITATION (IN 9 SEC.).

From solution as below: V = 350 cc.

Salts.	Na_2SO_4		Na_2SO_4 + 5NaCl	Na_2SO_4 + 10NaCl	K_2SO_4 + 10KCl.	
cc. 20 per cent. HCl.	0.2		0.2	1	0.2	
$BaSO_4$ (calc.)	2.0199	2.0224	2.1352	2.0069	2.0105	2.0223
$BaSO_4$ (found)..........	2.0142	2.0163	2.1354	2.0090	2.0089	2.0160
Chlorine[4]................	...	0.4	2.6	1.0	0.8	...
Chlorine (corr.)	...	—1.2	—7.5	—3.1	—2.5	—2.5
Alkali sulphate.	5.3	4.7	8.9	4.4	9.1	10.1
Do. (corr.)........ ...	3.7	3.3	6.2	3.0	3.7	4.1
Sy. (corr.)..	2.1	1.9	1.0	1.0	2.4	2.4
Vy. (corr.).	0.6	0.6	0.6	2.1	5.0	4.4
Sum of corrs	6.4	4.6	0.3	3.0	8.6	8.4
Deficit.......	5.7	6.1	—0.2	—2.1	1.6	6.3
	—0.7	1.5	—0.5	—5.1	—7.0	—2.1

---

[1] Presumably only Na_2SO_4 remained in the precipitate; chlorine was not tested for.

[2] Had an extraction with sulphuric acid, instead of water, been made, all would have been changed to sulphate.

[3] *Z. anal. Chem.*, 45, 31 (1906).

[4] After ignition the chlorine is doubtless present in the precipitate as sodium chloride; still it makes no difference whether it is regarded as combined with sodium or barium. The sodium is always more than equivalent to the chlorine and we may regard (1) all the chlorine as $BaCl_2$ and all the sodium as sulphate, or (2) all the chlo-

far superior to the ordinary slow precipitation. It should be stated that the conditions we followed were not exactly those recommended by Hintz and Weber. They used 1 cc. conc. hydrochloric acid in 450 cc., and, having previously diluted the reagent to 100 cc. and heated to boiling, poured it in all at once. We adopted the variations in the hope of greater uniformity. The results obtained are, in fact, similar to theirs, both in uniformity and accuracy. They are not so reliable as the corrected results when the precipitation is done slowly, but they are often surprisingly good.

Total Sulphuric Acid Occluded by Barium Sulphate Precipitates.

It is now evident that the total quantity of free sulphuric acid originally present in all barium sulphate precipitates is greater than that lost by volatilization; a part of it is held back by the barium chloride which the precipitates also retain, and an equivalent of hydrochloric acid is volatilized in its place. Although no part of the analytical problem, we regarded it as a matter of some interest to determine the total quantity of sulphuric acid occluded under various conditions. Accordingly, the volatile products were collected as usual and both the hydrochloric and sulphuric acids were determined in each. Table XIV shows the quantities of hydrochloric acid (in terms of silver chloride) which are lost by precipitates formed under stated conditions. Table XV gives, in parallel columns, the quantities of hydrochloric acid volatilized, in terms of sulphuric acid, and the quantities of sulphuric acid which are lost as such.

TABLE XIV.—EFFECT OF RATE OF PRECIPITATION ON CHLORINE[1] VOLATILIZED IN THE IGNITION OF PRECIPITATES

Chlorine (in mgs AgCl) in 2 grams precipitate.

Time of precipitation

	0.2 cc 20 per cent. HCl		1 cc 20 per cent HCl		5 cc 20 per cent HCl		10 cc 20 per cent HCl	20 cc 20 per cent HCl
NaCl	3–6 min.	9 sec	3–6 min	9 sec	3–6 min	9 sec	3–6 min	3–6 min
0	0.6	2.8	4.8	.	2.3	5.3	2.6	0.6
	...	. .	5.9	.	1.8	.	1.3	2.0
5	6.3	3.4	5.6	.		.	.	.
	3.1	4.0	5.0	.	.	.	. .	.
10	6.0		3.5	8.7		.	. .	.
	4.8	.	3.4	5.1	.		.	.

---

rine as NaCl and the rest of the sodium as sulphate. If a = Cl found and b = Na_2SO_4 extracted with sulphuric acid, the corrections would be:

$$(1)\ b\,\frac{BaSO_4 - Na_2SO_4}{Na_2SO_4} - a\,\frac{BaCl_2}{2Cl}. \qquad (2)\ \left[b - a\,\frac{Na_2SO_4}{2Cl}\right]\frac{BaSO_4 - Na_2SO_4}{Na_2SO_4} -$$

$$\frac{2NaCl}{2Cl}\,a = \frac{BaSO_4 - Na_2SO_4}{Na_2SO_4}\,b - \frac{BaSO_4 - Na_2SO_4 + 2NaCl}{2Cl}\,a,$$

which is identical with (1).

[1] This quantity equals the total quantity occluded in slow precipitations; it is less than the total in rapid precipitations.

TABLE XV —SULPHURIC ACID (IN MG) OCCLUDED BY 2 GRAMS PRECIPITATE

cc 20 per cent HCl	0 2			1 0			5 0			10 0			20.0		
Volatilized as	HCl	H_2SO_4	Total	HCl	H_2SO_4	Total	HCl	H_2SO_4	Total	HCl	H_2SO_4	Total	HCl	H_2SO_4	Total
Grams NaCl						A Slow Precipitation									
0	1 6	0 2	1 8	1 8	0 9	2 7	0 7	1 9	2 6	0 7	1 2	1 9	0 4	0 7	1 1
5	1 6	2 2	3 8	1 8	3 9	5 7		4 6							
10	1 8	3 4	5 2	1 2	5 2	6 4									
						B Rapid Precipitation									
0	1 2	0 3	1 5				1 8	0 2	2 0						
	1 3	0 3	1 6												
	1 0	0 2	1 2												
10				3 0	1 5	4 5									
				1 7	1 9	3 6									

A comparison of the figures for slow and rapid precipitation shows that the hydrochloric acid volatilized is not much influenced by the rate of precipitation, though it is usually a little greater when the precipitation is rapid The results on page 600 show, however, that the *total* chloride present in the precipitate is much increased by the rate at which it is thrown down It follows that rapidly formed precipitates must occlude less free sulphuric acid, and thus a rapid rate of formation reduces the volatility loss

The Correction of Sulphate Determinations.—The following tables (XVI-XVIII) contain a series of determinations of sulphur in sodium sulphate under stated conditions, giving the proper corrections for "solubility," occlusion, and volatility. From the horizontal lines designated "deficit" the original percentage loss may be seen to vary

TABLE XVI —CORRECTION OF SULPHATE DETERMINATIONS

Pptn from Na_2SO_4; V = 350 cc 0 1 cc. 20 per cent. HCl.

	1	2	3	4	Mean
$BaSO_4$ (calc)	2037 3	2051 0	2041 6	2016 3	. . ..
$BaSO_4$ (found)	2030 9	2046,1	2033 2	2010 0	. . . .
Na_2SO_4 (found)	8 7	7 1	9 1	8 3	8 2
Na_2SO_4 (corr.)	*6,1*	*5 0*	*6 4*	*5 8*	*5 7*
Sy (corr)	1 0	0 9	*1 0*	*1 0*	*1 0*
Vy (corr)	*0 3*	*0 3*	*0 3*	*0 3*	*0.3*
Sum of corrs	7 4	6.2	7.7	7.1	*7.0*
Deficit	6 4	4.9	8.4	6.3	*6.5*
Loss	—1 0	—1 3	0.7	—0.8	*0.8*
Percentage loss	0.05	0.07	0.03	0.04	*0.04*
Percentage error with average corr..	0.03	0.10	0.07	0.0	. . . .

Figures in italics in this and all subsequent tables include calculated corrections, also corrections not experimentally determined in the case under consideration.

In 4 the precipitate was boiled for 3 hours with 10 grams $BaCl_2$ in 300 cc. water.

from 0.25–0.79 per cent., while after correction the error falls to 0–0.15 per cent. In the great majority of cases it is 0.10 per cent. or less. The greater errors in all instances occur in determinations where the conditions were later found to be faulty.

TABLE XVII.—CORRECTION OF SULPHATE DETERMINATIONS.
Precipitation from Na_2SO_4; V = 350 cc.: 0.2 cc. 20 per cent. HCl.

	1	2.	3.	4.	5.	6.
$BaSO_4$ (calc.)	2002.2	2000.0	2040.7	2037.4	1995.4	2044.5
$BaSO_4$ (found)	1996.7	1992.5	2035.7	2029.4	1985.5	2032.6
Na_2SO_4 (found) .. .	9.2	9.8	11.9	11.6	11.3	10.5
Na_2SO_4 (corr.) ..	*6.4*	*6.9*	*8.3*	*8.1*	*7.9*	*7.3*
Sy. (corr.).	*1.0*	*1.0*	0.6	0.7	*1.0*	*1.0*
Vy. (corr.) .	*0.6*	*0.6*	*0.6*	*0.6*	*0.6*	*0.6*
Sum of corrs.... .	8.0	8.5	9.5	9.4	9.5	8.9
Deficit	5.5	7.5	5.0	8.0	9.9	11.9
Loss . .	—2.5	—1.0	—4.5	—1.4	0.4	3.0
Percentage loss . ..	0.12	0.05	0.22	0.07	0.02	0.15

3 and 4 filtered in $^1/_2$ hour; volatility loss a little doubtful.
5 and 6 filtered through Gooch crucible.

TABLE XVIII.—CORRECTION OF SULPHATE DETERMINATIONS.
Precipitation from Na_2SO_4. V = 350 cc.

cc. 20 per cent. HCl.	1. 0.5	2. 1.0	3. 1.0	4. 1.0	5. 1.0	6. 1.0
$BaSO_4$ (calc.).	2020.6	2052.8	2020.1	2031.9	1997.5	2026.3
$BaSO_4$ (found).	2013.2	2044.2	2008.1	2016.1	1986.9	2011.2
Na_2SO_4 (found)....	8.0	. .	6.9	6.9	8.2	8.9
Na_2SO_4 (corr.)	*5.6*	*5.5*	*4.9*	*4.9*	*5.8*	*6.3*
Sy. (corr.)	1.0	1.6	3.0	6.4	4.4	4.3
Vy. (corr.)........	*2.2*	*2.2*	*2.2*	*2.2*	*2.2*	*2.2*
Sum of corrs. . .	8.8	9.3	10.1	13.5	12.4	12.8
Deficit......... ..	7.4	8.6	12.0	15.8	10.6	15.1
Loss	—1.2	0.7	1.9	2.3	—1.8	2.3
Percentage loss......	0.06	0.03	0.10	0.12	0.09	0.11

Table XIX gives corrected determinations of sulphur in the presence of various quantities of sodium chloride—a very common case in practice. The errors range from 0.8–1.8 per cent. before correction and are reduced by correction to from 0.03–0.14 per cent. with a mean error of only 0.08 per cent.

The determinations given in Tables XVI, XVII and XVIII are uniform enough to make satisfactory corrections by the use of the constants which are the means of the different determinations. Thus, in Table XVIII, the constants are, for 2 grams precipitate, volatility, Vy., = 2.2 mg.; occlusion, Oc. = 5.1. For solubility in this case individual cor-

TABLE XIX.—CORRECTION OF SULPHATE DETERMINATIONS WHEN CHLORIDES ARE PRESENT

Precipitation from Na_2SO_4

	0.2 cc 20 per cent HCl			1.0 cc 20 per cent HCl				
Grams NaCl	5.0	5.0	10.0	3.0	5.0	8.0	10.0	10.0
$BaSO_4$ (calc.)	2011.5	2002.8	2021.[illegible]	2007.4	1977.0	2013.7	2015.3	1990.9
$BaSO_4$ (found)	1991.4	1986.7	1997.4	1990.2	1954.3	1990.3	1991.5	1955.0
Na_2SO_4 (found)	17.1	17.5	17.8	11.4	13.5	11.2	10.6	23.6
Na_2SO_4 (corr.)	*12.0*	*12.3*	*12.5*	*8.0*	*9.5*	*7.9*	*7.4*	*16.7*
Sy (corr.)	1.1	0.7	2.3	*1.6*	*1.6*	*1.6*	*1.6*	*2.7*
Vy (corr.)	*5.3*	*5.3*	*8.8*	*6.0*	*10.0*	*11.8*	*13.7*	*13.7*
Sum of (corr.)	18.4	18.3	23.6	15.6	21.1	21.3	22.7	33.1
Deficit	20.1	16.1	24.3	17.2	22.7	23.4	23.8	35.9
Loss	1.7	—2.2	0.7	1.6	1.6	2.1	1.1	2.8
Percentage loss	0.08	0.11	0.03	0.08	0.08	0.10	0.05	0.14

rections are required because Experiments 1 and 2 were filtered after 18 hours, the rest in a short time. In one or two instances, also, a little fine precipitate was washed over the top of the paper and was recovered in the filtrate, thus increasing the usual correction. In Table XVI, the average corrections are Vy. = 0.3 mg., Oc. = 5.7 mg., Sy. = 1.0 mg., total = 7.0 mg. In Table XVII, the corrections are: Vy. = 0.6 mg., Sy. = 1.0, Oc. = 7.5, total = 9.1. Here the average cannot be applied quite so well as the individual corrections. In Table XIX, which includes cases where sodium chloride is originally present, Vy. and Oc. are much larger and both are quite sensitive to conditions. It is wise in such cases to apply individual corrections, making a duplicate precipitation under identical conditions, on which the volatility is determined.

B. The Precipitation of Potassium Sulphate by Barium Chloride.

The same sources of error occur in precipitating barium sulphate from potassium as from sodium sulphate.

Losses Due to "Solubility."—The loss from solubility is of the same order of magnitude and is increased only very slightly by the addition of potassium chloride to the sulphate solution, in spite of the statements to the contrary, already quoted (see p. 592). It is not surprising that many who have noted large errors in the determination of sulphur where alkali chlorides are present should have suspected that these were due to solubility. Of course, if this view is correct, the loss will depend, not on the quantity of the precipitate, but on other conditions, chiefly the volume and composition of the solution. Our results show, on the contrary, that the errors depend on the quantity of the precipitate, *i. e.*, they are percentage errors.

A weighed quantity of one of our precipitates, which had been heated to redness, was put into a beaker, to which was added 10 g. potassium chloride, 350 cc. water, and 0.2 cc. 20 per cent. hydrochloric acid. This was heated to boiling and kept on the steam bath, with occasional stirring, for several hours. Then it was left to stand over night. Next morning it was filtered on a small filter, washed free of chlorine and weighed.

	Gram		Gram
$BaSO_4$ taken	0.0683	Found in precipitate	0.0668
$BaSO_4$ found	0.0694	" " filtrate	0.0026
$BaSO_4$ loss	0.0011		0.0694

Objection might be taken to the use of a *heated precipitate* here, on the ground that there might be an irreversible change in barium sulphate on heating, leaving finally another phase of different solubility. A microscopic examination made by Dr. F. E. Wright, of this laboratory, showed that the index of refraction of the substance was little affected by heating. It remained about 1.63, the value for natural barite, and in no other respect did the substance appear to be changed, except that the crystallization became somewhat coarser. Still, to leave no doubt in the matter, further experiments were tried on the unheated substance.

A weighed quantity of pure dry potassium sulphate was dissolved in 350 cc. water, with given quantities of potassium chloride and hydrochloric acid. The solutions were precipitated boiling hot by 0.5 cc. more than the calculated quantity of barium chloride, kept hot a few hours and allowed to stand over night, after which the procedure was similar to that in the experiment just described.

TABLE XX.—DIRECT DETERMINATION OF THE SOLVENT INFLUENCE OF POTASSIUM CHLORIDE ON BARIUM SULPHATE

Precipitation of K_2SO_4 + KCl + 0.2 cc. 20 per cent. HCl, V = 350 cc.

KCl Grams	K_2SO_4 Gram	$BaSO_4$ calc Gram	$BaSO_4$ found in ppt Gram	$BaSO_4$ found in filtrate Gram	Loss Gram.
5	0.0689	0.0923	0.0896	0.0013	0.0014
10	0.0873	0.1169	0.1128	0.0014	0.0027

TABLE XXI.—LOSSES (IN MG.) DUE TO SOLUBILITY OF $BaSO_4$.

Precipitated from solutions containing sulphates and chlorides (as below), and 0.2 cc. 20 per cent. HCl. Original volume 350 cc., total volume 650–700 cc.

From solutions containing	Na_2SO_4 + NaCl (as below)			K_2SO_4 + KCl (as below)			$(NH_4)_2SO_4$ + NH_4Cl (as below)		
	0	5 gms.	10 gms	0	5 gms.	10 gms	0	5 gms	10 gms
$BaSO_4$ (in mg.).	0.9[1]	1.1	2.7	1.0	2.3	2.6	1.4		1.4
In filtrate.. . .	...	0.7	2.3	0.8	2.6	2.8	1.2	.	.
	..		.		.	2.8	1.2	..	.
	..	...	.	..	1.3[2]	1.4[2]	..	1.2[2]	1.4[2]
Mean...... .. .	0.9	0.9	2.5	0.9	2.1	2.4	1.2	1.2	1.4

[1] This value is the mean of those given in Table I, line 1.

[2] In these determinations the total quantity of $BaSO_4$ was less than 0.1 gram; in all the others, it amounted to 2.0 grams.

Thus the barium sulphate recovered from the filtrate is not only of the same order of magnitude as it is where no alkaline chloride is present, but the total loss is greatly reduced when the mass of the precipitate is reduced. The evidence is very clear that potassium chloride has no influence on the solubility of barium sulphate within the limits of error of this method Table XXI compares the solubility losses occasioned by the chlorides of sodium, potassium, and ammonium (which will be treated in detail in the next section), with the losses found when no chlorides are originally present.

Occlusion of Potassium Sulphate—Barium sulphate occludes sodium and potassium sulphates in about equal quantity when the conditions are similar. The correction for potassium sulphate, 59/174 = $(BaSO_4—K_2SO_4)/K_2SO_4$, is, however, evidently less The quantity of potassium sulphate obtained from a precipitate by a single extraction with sulphuric acid (see p. 593) is about 80 per cent of the total quantity

		Mg	Mg	Mg.
1st extraction K_2SO_4	=	16 1	19 1	3 4
2d extraction K_2SO_4	=	3 3	4 8	0 7

It will be within the limits of experimental error, since the total quantities are so small, if we make a single extraction and add to the quantity obtained 25 per cent. more. The corrections in Tables XXIII and XXIV are made in this way.

Loss by Volatilization.– Precipitates from potassium sulphate lose notably more on ignition than precipitates from sodium sulphate. Even with very weak acid (0 2 cc. 20 per cent in 350 cc.) and no potassium chloride in the original solution, the losses are 0 3 per cent. from this source alone if the precipitation is slow; with 10 grams potassium chloride and the same concentration of acid, the losses reach 0 7 per cent., and with 10 grams potassium chloride and 1 cc. 20 per cent hydrochloric acid, 1 5 per cent. Others have noticed greater losses when potassium chloride was present, but have ascribed them to increased solubility. The data are tabulated in Table XXII.

Chlorine.—The chlorine is negligible in ignited precipitates from potassium sulphate, if the precipitation is slow.

Correction of Sulphur Determinations.—The corrected results in Table XXIII, on the sulphur in potassium sulphate, leaves little to be desired. The losses vary from —0.07 per cent. to +0 07 per cent. If potassium chloride is present in quantity, the important conditions to be followed are a small quantity of free acid and close attention to rate of precipitation. In Tables XXIV, Nos. 3, 5, 6, and 7, the rate was carefully regulated by attaching to the burette a capillary tip, both in the determination itself and in the duplicate precipitations for the determination of the volatility loss. Although the errors are large, the final losses vary, from —0.07 to +0 06 per cent. Nos. 1, 2, and 4 were done at an earlier stage of the work; they were precipitated more rapidly and without measuring the rate. The corrections which were made on precipitates slowly formed are therefore not applicable to them; the sum of the corrections is greater than the deficits, as our study of the composition of barium sulphate precipitates shows should be the case

TABLE XXII —EFFECT OF KCl ON THE LOSS OF SULPHURIC ACID BY VOLATILIZATION

Losses in mg $BaSO_4$ per 2 grams precipitate.

Grams KCl	cc 20 per cent HCl	Mg	
0	0 2	6 4	
5	0 2	13 7	14 3
5	1 0	23.9	21.8
10	0 2	18 1	17 6
10	1 0	30 7	

TABLE XXIII —CORRECTION OF SULPHATE DETERMINATIONS

Precipitation from K_2SO_4, V = 350 cc , 0 2 cc 20 per cent HCl

$BaSO_4$ (calc)	2002 8	2002 7	2013 0	2006 7
$BaSO_4$ (found)	1992 8	2009 3	2002 6	1995 2
K_2SO_4 (found)	10 1	11 4		
K_2SO_4 (corr)	*4 1*	*4 7*	*4 4*	*4 4*
Sy (corr)	*1 0*	0 8	*1 0*	*1 0*
Vy (corr)	*6 4*	*6 4*	*6 4*	*6 4*
Sum of corrs	11 5	11 9	11 8	11 8
Deficit	10 0	13 4	10 4	11 2
Loss ..	—1 5	1 5	—1 4	—0 6
Percentage loss	0 08	0 07	0.07	0 03

TABLE XXIV.—CORRECTION OF SULPHATE DETERMINATIONS

Precipitation from K_2SO_4 + KCl; V = 350 cc , 0 2 cc 20 per cent HCl.

	5 grams KCl			10 grams KCl			
No	1	2	3	4	5	6	7
$BaSO_4$ (calc)	2016 4	2017 2	2000 3	2019 2	1963 3	1998 5	2000 2
$BaSO_4$ (found)	2000 0	1997 7	1978 9	2000 3	1937.5	1969 4	1972 7
K_2SO_4 (found)	14 6	16 1	11 1	10 2	15 7	19 1	14 2
K_2SO_4 (corr)	*6 0*	*6 6*	*4 5*	*4.2*	*6 4*	*7 8*	*5 8*
Sy (corr.)	2 3	2 6	2 1	2 8	2 6	2 8	2 4
Vy. (corr)	14 3	*14 3*	14 3	*18 1*	18 1	*18 1*	18 1
Sum of corrs . .	22.6	23 5	20 9	25 1	27 1	28 7	26 3
Deficit . .	16.4	19 5	21.4	18 9	25 8	29 1	27 5
Loss	—6.2	—4 0	0 5	—6 2	—1 3	0 4	1 2
Percentage loss .	—0 31	—0 20	—0 02	—0 31	—0 07	0 02	0 06

C. Precipitation of Ammonium Sulphate by Barium Chloride.

So far as the composition of a precipitate from ammonium sulphate is concerned, it does not differ essentially from precipitates previously considered, *i e.*, it contains ammonium sulphate, "free" sulphuric acid, and chlorine in quantities which increase with the rate of precipitation. This case differs from all others, however, in one respect—that the ammonium sulphate in it is almost entirely volatile at a red heat, therefore the loss from occlusion is much greater than it is in other cases.

The ammonium sulphate used in all the experiments described was entirely volatile at a red heat. It was dried to a constant weight at 130°.[1]

Losses Due to Solubility.—The influence of ammonium chloride on the solubility of barium sulphate has been treated exactly like the influence of potassium chloride, and it is shown in Table XXV that when small quantities of sulphur are determined in solutions containing ammonium chloride the total losses are almost negligible; hence the great losses when the quantities of sulphur are large could not be due to solubility

TABLE XXV —DIRECT DETERMINATION OF THE SOLVENT INFLUENCE OF AMMONIUM CHLORIDE ON BARIUM SULPHATE

Precipitation of $(NH_4)_2SO_4 + NH_4Cl$ + 0 2 cc 20 per cent HCl, V = 350 cc

NH_4Cl Grams	$(NH_4)_2SO_4$ Gram	$BaSO_4$ calc Gram	$BaSO_4$ found in ppt Gram	$BaSO_4$ found in filtrate Gram	Loss
5	0 0147	0 0259	0 0253	0 0012	—0 0006
10	0 0281	0 0495	0 0471	0 0024	0

Ammonium Sulphate Occluded by Barium Sulphate—This was determined on 2 gram precipitates as follows:

The precipitate dried at 105° was dissolved in about 15 cc. concentrated sulphuric acid with gentle warming, cooled and poured into about 250 cc. cold water and filtered. The filtrate was then distilled with a slight excess of pure soda, and the distillate collected in excess (10 cc. 20 per cent.) of dilute hydrochloric acid. The latter was evaporated almost to dryness on the steam bath, then further with addition of platinum chloride. The ammonium chloroplatinate was separated with alcohol and dried at 130° in the usual way. The ammonium was calculated by the use of the empirical factor 0 081.[2] Not improbably one extraction with sulphuric acid may fail to remove the total quantity of ammonium sulphate, but, judging from experience with sodium and potassium sulphates, the amount left in the precipitate cannot be large, and since the exact quantity is not needed for correction purposes, this point was not settled.

An inspection of the data in Table XXVI shows that the losses from occlusion ($BaSO_4$ equiv.) are equal to about 1 2 per cent. of the total sulphur under the above conditions. The quantity of ammonium sulphate occluded by the precipitate varies little with the rate of precipita-

---

[1] See Lunge and Stierlin, *Loc. cit.*

[2] See Treadwell, "Quantitative Analysis" (translated by Hall), p. 54.

TABLE XXVI.—OCCLUSION OF AMMONIUM SULPHATE (IN MG.) BY BARIUM SULPHATE.
Precipitation from 1.14 grams $(NH_4)_2SO_4$ + NH_4Cl + 0.2 cc. 20 per cent. HCl; V = 350 cc.

	Time of precipitation					
	5 g NH_4Cl.		10 g NH_4Cl.		10 g NH_4Cl. 4 min	
	6 min	9 sec	6 min	9 sec.		
$(NH_4)_2PtCl_6$ obtained ..	48.8	45.9	51.6	50.4	5.0	4.5
Blank for reagents . . .	2.2	2.2	2.2	2.2	2.2	2.2
	46.6	43.7	49.4	48.2	2.8	2.3
$(NH_4)_2SO_4$ equiv. .	13.8	13.1	14.7	14.3	0.8	0.7
$BaSO_4$ equiv ...	24.4	23.1	25.9	25.2		

tion; it is slightly less when the rate is rapid, just as it is with sodium and potassium salts. After the precipitates have been ignited, as the table shows, they contain only a trace of ammonium sulphate. It may be noted in passing that we have here a simple method for preparing pure barium sulphate.[1]

Loss by Volatilization.—We have seen in the preceding paragraph that all but a trace of the occluded ammonium sulphate is lost by heating, and, since this should have been converted into barium sulphate, the loss is comparatively large. The *total* loss by volatilization is still greater, because these precipitates, in complete analogy with others which we have considered, contain also "free" sulphuric acid. Table XXVII gives the losses due to volatilization. The column headed "free sulphuric acid" is obtained by difference. The determination of the total volatility gave a good deal of trouble. Very low results were obtained with the tubulated crucible. This may have been due to the retention of some of the sulphate by the sodium tungstate used to seal the joint. The platinum combustion tube and boat gave, when sufficient heat was applied, nearly correct results. As previously stated, two bulbs should be used for complete absorption.

TABLE XXVII.—LOSSES BY VOLATILIZATION (IN MG.) FROM 2 GRAMS PRECIPITATE
Precipitation from $(NH_4)_2SO_4$ + NH_4Cl and 0.2 cc. 20 per cent. HCl; V = 350 cc.

0 gram NH_4Cl			5 grams NH_4Cl			10 grams NH_4Cl		
Due to $(NH_4)_2SO_4$	Due to "free" H_2SO_4	Total	Due to $(NH_4)_2SO_4$	Due to "free" H_2SO_4	Total	Due to $(NH_4)_2SO_4$	"Due to free" H_2SO_4	Total
		11.2	24.4	3.9	28.3	25.9	11.3	37.2
		11.1	24.4	5.5	29.9	25.9	9.6	35.5

Correction of Sulphate Determinations.—The following determinations in Table XXVIII will serve to show the magnitude of the losses, when sulphur is determined in ammonium sulphate, with or without ammonium chloride. It hardly need be said that these errors, reaching 2 per cent. at the maximum, would be very considerably increased in the presence

---

[1] These two precipitates were ignited before testing for ammonium.

TABLE XXVIII.—CORRECTION OF SULPHATE DETERMINATIONS

Precipitation from $(NH_4)_2SO_4 + NH_4Cl$ V = 350 cc 0.2 cc 20 per cent HCl

	0 gram NH_4Cl		5 grams NH_4Cl	10 grams NH_4Cl	
$BaSO_4$ (calc.)	2014.2	2015.4	2015.2	2018.4	2013.8
$BaSO_4$ (found)	2000.6	2000.6	1984.2	1979.2	1972.1
Corr. for Vy	11.2	11.2	28.3	37.2	37.2
Corr. for Sy	*1.4*	*1.4*	*1.4*	*1.4*	*1.4*
Sum of errors	12.6	12.6	29.7	38.6	38.6
Deficit	13.6	14.8	31.0	39.2	41.7
Loss	1.0	2.2	1.3	0.6	3.1
Percentage loss	0.05	0.11	0.07	0.03	0.15

of more free acid. These data also make it evident why ammonium salts should be avoided, if possible, in solutions where sulphur is to be determined. Nevertheless, although the errors are large, it will be noticed in the table that the sum of the corrections very nearly make up the deficits found in actual determinations. It is therefore possible to get very good results in the presence of ammonium salts by applying the proper corrections.

D. Precipitation of Magnesium Sulphate by Barium Chloride.

Hulett and Duschak[1] found that magnesium sulphate gave, with barium platinocyanide, precipitates which agreed in weight with the calculated quantity. Their explanation was that the impurities in precipitates formed from sulphuric acid and barium chloride were due to the formation of complex salts by the union of intermediate ions; *e. g.*

$$2BaCl' + SO_4'' = \begin{matrix} Ba-Cl \\ Ba-Cl \end{matrix}\Big\rangle SO_4 \text{ and } 2HSO_4' + Ba'' = \begin{matrix} HSO_4 \\ HSO_4 \end{matrix}\Big\rangle Ba.$$

To us it seemed not improbable that the purity of the precipitates from magnesium sulphate might be due to the fact that barium sulphate has not the power to occlude magnesium sulphate while it can occlude the sulphates of the alkalies. If this view is correct, any salt of barium would do as well as the platinocyanide. The sequel shows that barium chloride, at least, gives similar results.

A standard solution of magnesium sulphate was prepared in the following manner. A solution of sulphuric acid of about the right strength was titrated against pure anhydrous sodium carbonate (heated to 300°). This was then neutralized by pure magnesium oxide and diluted to a definite weight. Details follow:

58.470 grams H_2SO_4 soln. required 1.0495 grams Na_2CO_3

55.946 grams H_2SO_4 soln. required 1.0042 grams Na_2CO_3

The titration was made at boiling temperature using phenolphthalein as indicator. Making corrections for buoyancy of the air,

---

[1] *Loc. cit.*

1 gram sol. = 0.016589 gram H_2SO_4 or 0.039488 $BaSO_4$.
1 gram sol. = 0.016591 gram H_2SO_4 or 0.039500 $BaSO_4$.

500.05 grams of this solution were now transferred to a platinum basin and evaporated with magnesium oxide (which had been especially freed from lime, sulphuric acid and water) until litmus paper showed that the solution was neutral. The undissolved excess of magnesium oxide was filtered off and thoroughly washed. It retained after washing 0.0173 gram SO_3. $BaSO_4$ found = 0.0503. The solution with washings was cooled and again diluted in a tared flask to a given weight, *viz.* 500.17 grams. After making corrections for buoyancy and subtracting the sulphur found with the undissolved magnesia, 1 gram solution = 0.039384 gram $BaSO_4$.

The results in Table XXIX are all obtained by the slow precipitation of weighed quantities of this standard solution under the same conditions as are found described on page 590. These data reveal the fact that very little magnesium sulphate is found in the precipitate, and show that the errors are much smaller than they are with the alkali sulphates. The volatility loss was a mere trace, immeasurable in three instances; in one case 0.3 mg. barium sulphate was found. In accord with this the chlorine is a little higher, though always less than 1 mg. As seen from the table, the original errors range from 0.01 to 0.21 per cent. in seven instances, while one result is 0.27 per cent. low.

TABLE XXIX.—CORRECTED RESULTS FOR $MgSO_4$.

	0.2 cc. 20 per cent HCl.		1 cc 20 per cent HCl.				2 cc. 20 per cent. HCl.		Average.
Grams $MgSO_4$ soln.	51.265	50.697	50.991	51.199	50.283	50.301	51.384	49.882	
$BaSO_4$ calc.	2019.8	1996.6	2001.2	2015.1	1980.3	1980.1	2022.3	1964.6	.
$BaSO_4$ found...	2019.6	1998.0	1995.7	2013.6	1978.8	1980.8	2018.0	1962.4	. .
Deficit.........	0.2	—1.4	5.5	1.5	1.5	—0.7	4.3	2.2	2.1
$MgSO_4$ in ppt...	2.9	3.1	2.0	1.7	3.4	.	1.3	.	.
Cl in ppt.	0.9	0.8	..	0.9	0.8	..	0.6	....	.
Vy. (corr.)	0	0	0	0	0	0	0	0	...
$MgSO_4$ corr. . ..	2.7	2.9	1.9	1.6	3.2	2.3	1.2	2.3	...
$BaCl_2$ calc.	3.6	2.3	2.3	2.6	2.3	2.3	1.8	2.3	...
Sy. (corr.)	1.2	1.2	1.2	1.2	1.2	1.2	2.0	2.0	...
Loss..........	—1.1	—3.2	4.7	1.3	—0.6	—1.9	2.9	0.2	2.0

The results have been corrected for solubility, which was determined with two concentrations of acid, for magnesium sulphate and for chlorine. As shown on pages 602-3, it makes no difference whether we assume that magnesium chloride + magnesium sulphate are present, or that all the magnesium is in the form of sulphate and the chlorine in the form of barium chloride. The corrected results are only a trifle better than the uncorrected.

The Effect of Nitrates on the Precipitation of Barium Sulphate.

According to statements found in the literature,[1] nitrates must removed from solutions in which sulphur is to be determined, otherwise the results are too high Our work confirms these assertions We have tried only the nitrate of sodium, but the same is probably true of potassium nitrate. Table XXX shows that when as little as 1 g of nitrate is contained in 350 cc. solution, the results are nearly 0 5 per cent. too high Five grams nitrate caused an error of 0 8 per cent and 10 grams nitrate had practically the same effect The cause of the error is not far to seek The table shows that the precipitates contain an unusual amount of sodium. One of them when boiled with water, gave up free alkali very slowly Evidently, the precipitate occludes the nitrate, which forms caustic soda on ignition On account of the hygroscopic nature of the impurity, the readiness with which it attacks platinum, and, moreover, the readiness with which it is avoided, it was not thought worth while to study this subject any further It has been suggested that the low results obtained in the determination of sulphur might be compensated by the addition of the correct amount of nitrate to the solution before it is precipitated. A fair degree of approximation might perhaps be reached in this way.

---

[1] Treadwell, "Quantitative Analysis" (translated by Hall), p. 281; Folin, *J. Biochem.*, 1, 145 (1906).

TABLE XXX--EFFECT OF NITRATES ON SULPHATE DETERMINATIONS

Results for Na_2SO_4 + $NaNO_3$ Amount of 20 per cent HCl = 0 2 cc

	Grams $NaNO_3$			
	1	2	5	10
$BaSO_4$ calc	2027 5	1968 8	2030 3	2057 5
$BaSO_4$ found	2036 7	1982 1	2046 3	2072 2
Na_2SO_4 found	14 6	16 5		30 1
Sy (corr)				1 6
Surplus (uncorr)	9 2	13 3	16 0	14 7

Nature of the Precipitate.

We have seen that barium sulphate precipitates even when thrown down from solutions of rather simple composition are, nevertheless, themselves pretty complex. The form in which the impurities are held in the precipitate is a question worthy of interest. The facts indicate that not all of them sustain the same relation to it. The barium chloride, for example, is present in very small quantity (about 0 15 per cent.) in slowly formed precipitates, reaching several times that quantity in those which are rapidly formed. Now, as rate of formation is a condition which especially governs the fineness of the precipitate, and the finest precipitates contain the greatest amount of this impurity, it is natural to conclude that we have here a case of adsorption. Hulett and Duschak made similar observations in the precipitation of barium chloride by sulphuric acid. Rapidly formed, fine-grained precipitates contained the most barium chloride; one in particular, which was formed very slowly indeed, contained only 0.03 per cent.

of chlorine (about 0.08 per cent. barium chloride). If the substance were held in a purely mechanical way, one would expect all the impurities to be increased, diminished or removed by the same conditions. This, as we have seen, is not the case. It is equally difficult to see how the alkali sulphate in the precipitate can be retained mechanically. Not only are the different impurities differently affected by the same conditions, but the absorption is a markedly selective phenomenon. No alkali chloride seems to be taken up, nor are all the sulphates. The sulphates of sodium, potassium, ammonium, ferric iron, and probably aluminium,[1] are absorbed, while magnesium sulphate (see p. 613) is scarcely absorbed at all. The selective nature of the absorption indicates a solid solution The fact that barium sulphate has an affinity for other sulphates is in accord with this What we may call the secondary conditions seem to change comparatively little the quantity of the sulphate which is taken up. After a precipitate has been ignited the greater part of the soluble sulphate may be extracted by water (Table XII).

It is not unusual to find that the solubility of one salt in another decreases markedly with rise in temperature, but one would expect the system to return to its former state on cooling. The rapidity of the cooling, however, might prevent this. On the other hand, the mechanical conception would explain this fact as well. The ignition might be supposed to disrupt compact grains of the precipitate, thus exposing the soluble impurities to the action of the solvent.

The "free" sulphuric acid in the precipitate may be supposed to have been dissolved in the form of acid sulphate of the alkali metal. The quantity decreases much with rapid precipitation, which may mean that the fine-grained material is changed more readily by the barium chloride, on standing in the supernatant liquid. We know that the sodium sulphate changes somewhat also, but to a less extent.

At present there seems to be little prospect of adding to our knowledge of such fine-grained substances by microscopic investigation, so that we are not even certain of the homogeneity of the precipitates, and we are free to confess, in conclusion, that the facts we have accumulated are insufficient to decide the question of their true nature.

Summary.

1. The errors in the determination of sulphur in soluble sulphates have been investigated for those cases which most frequently occur in experimental work. Solutions of sodium, potassium, ammonium and magnesium sulphates have been studied, both in a state of purity and in the presence of varying quantities of hydrochloric acid and alkali chlorides. In a few systems the influence of sodium nitrate has also been studied.

---

[1] Schneider, *Z. physik. Chem.*, 10, 425 (1895); Creighton, *Z. anorg. Chem*, 63, 53 (1909).

2. The most important sources of error are three in number, one arising from the solubility of the precipitate and the others from its composition. Two minor sources may also be mentioned.

a. The error from solubility depends chiefly on the quantity of free acid present. Contrary to the common belief, we find that the chlorides of sodium, potassium, and ammonium exercise a hardly appreciable influence on it. Under easily regulated conditions (0.2 cc. 20 per cent. HCl in 350 cc. original solution) it amounts to 1–2 mg. only. It is self-evident that this error (almost negligible for precipitates of 1 g. or more) becomes increasingly important, the smaller the precipitate.

b. All barium sulphate precipitates carry down with them quantities of the alkaline sulphates, varying with many conditions. In the case of pure acidulated sulphates, this quantity is not far from 0 5 per cent. It is especially affected by alkali chlorides, and may be more than doubled in this way. The correction depends of course on the atomic weight of the alkali metal. About 0 75 per cent. is the maximum quantity of ammonium sulphate absorbed by precipitates under conditions which have been investigated by us; the correction for it is, however, comparatively large (1.25 per cent.), because ammonium sulphate is entirely volatilized when the precipitate is ignited. Magnesium sulphate is scarcely absorbed at all by barium sulphate. The peculiar selective adsorption which barium sulphate exhibits, suggests the formation of solid solutions. The evidence on the subject is, however, too meager for a proof.

c. Barium sulphate, when precipitated from alkali sulphates, always occludes a certain amount of "free" sulphuric acid, which is probably taken up as acid sulphate of the alkali metal. It arises, of course, from the free acid added to the original solution and increases with it up to a certain point. Alkali chlorides decidedly increase the amount of it, and in the presence of much of the latter, it becomes the chief source of error. Aside from one or two qualitative observations, this loss seems to have been thus far entirely overlooked. It is greater for potassium than for sodium sulphate solutions. In one case a solution of the former containing 10 grams KCl and 5 cc. 20 per cent. HCl in 350 cc. lost 1.7 per cent. in this way.

d. All barium sulphate precipitates contain barium chloride. If the precipitation is made slowly (3–6 min. for 2 grams $BaSO_4$), the amount of this is only about 0.15 per cent. in the unignited precipitate, and since all but a trace of it is eliminated as hydrochloric acid during ignition, it is not a source of error. When a precipitate is very rapidly formed the amount of the barium chloride is multiplied several times and the chlorine is no longer entirely eliminated on ignition. The more rapid the precipitation, the finer the precipitate, and since the barium chloride retained increases with the fineness, we regard it as probably held by adsorption. The other impurities are diminished by rapid precipitation.

e. Sodium nitrate, and probably other nitrates also, are occluded by barium sulphate, giving results which are therefore too high.

3. An exact determination of sulphur, so far as we know, can only be done by correcting for the above-named errors. Nitrates are to be avoided, also chlorides and ammonium salts as far as possible. Corrections for occlusion and solubility can be made directly, but for volatility, unless one has a specially constructed platinum apparatus, a duplicate precipitation must be made under identical conditions.

We recommend the following conditions: Acidulate the solution (V = 350 cc.) with 2 cc. 2 per cent. hydrochloric acid and heat to boiling. Precipitate slowly (about 4 min. for 2 grams precipitate) with constant stirring. The rate may be regulated by a burette with a capillary tip attached. Let the precipitate stand 18 hours before filtering; the losses from occlusion and volatility are both considerably higher when the filtration is done immediately. Filter on paper and wash till 25 cc. of the washings show a barely perceptible opalescence with silver nitrate. Burn very slowly and carefully and heat over the burner to a constant weight. To this result should be applied the corrections for the errors just discussed. If the solution contains only alkali sulphate and known quantities of alkali chloride and hydrochloric acid, and if the directions above are carefully followed, the correction constants determined by us may be applied. A more accurate result might perhaps be reached by the application of corrections experimentally determined for the case in hand. Detailed methods for these are given in the body of the paper. In unknown mixtures of alkali chlorides the corrections must, of course, be actually determined. To correct for the occlusion in such cases it would only be necessary to take the weight of the mixed alkali sulphates extracted from the precipitate, to convert them into barium sulphate and weigh; the difference between the weights of the barium sulphate and the mixture is the correction. A carefully corrected determination of sulphur for the cases given should be accurate to 0.1 or 0.2 per cent. of the total sulphur. A very good uncorrected determination may be obtained by precipitating *rapidly*, but it is due to partial compensation of variable errors, and is not in any case so reliable as one which is made by slow precipitation and corrected as described.

The authors wish to express their thanks to Dr. W. F. Hillebrand for reading the manuscript of this paper, and for suggesting a number of emendations.

GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.

ON THE FORMATION OF DOUBLE SALTS.

By H. W. Foote.

Received February 22, 1910.

The object of this investigation was to determine the influence of various organic solvents on the formation of certain double salts which yield hydrates when crystallized from water. The facts regarding simple salts are much better known than those regarding double salts. Thus, Menschutkin,[1] among many others, has shown that an organic solvent may replace the water of crystallization in many cases, so that a salt crystallizing at a given temperature with a certain number of molecules of water will crystallize from an organic solvent with the same number—sometimes with a smaller number—of molecules of that solvent. Again, the water of crystallization of a simple salt can ordinarily be removed by suitable means, leaving the stable anhydrous salt, and the water of crystallization is in general not necessary in order that the salt itself should be formed. Whether the water, or more generally the solvent, of crystallization is necessary in order that a double salt shall form and whether the solvent affects the type of salt formed, has been but little investigated. Almost the only work on the formation of double salts from non-aqueous solutions has been done recently by Cambi,[2] but it is somewhat difficult to draw conclusions from his work which apply to the present problem, as it is not certain in the cases investigated by him that all the double salts capable of forming at a given temperature from any one solvent are known.

For the present investigation, the double salts of mercuric chloride with sodium and potassium chlorides were chosen. The double salts which these chlorides form from water at 25° have already been determined.[3] These salts, all containing water of crystallization, have the following composition:

$NaCl.HgCl_2.2H_2O$
$2KCl.HgCl_2.H_2O$
$KCl.HgCl_2.H_2O$
$KCl.2HgCl_2.2H_2O$

Mercuric chloride is much more soluble in some organic solvents than it is in water, and the alkali chlorides have an appreciable solubility in these solvents when mercuric chloride is present. Absolute alcohol was used as solvent for sodium and mercuric chlorides and both absolute alcohol and acetone were used when potassium chloride was present. The alcohol was purified by treating with sodium and distilling. The acetone was dried over anhydrous copper sulphate and distilled.

The same solubility method has been used for determining double salts that was previously used in determining the double mercuric chlorides formed from water. By this method, all salts forming from a solvent at a given temperature can be definitely determined. Varying proportions of the salts and solvent were mixed together in small bottles with ground glass stoppers. The salts were weighed and the volume of liquid measured to serve as guides in making other mixtures. The salts very often formed in lumps when first brought into contact with the liquid, due to the formation of double salts. When the lumps could not be broken by shaking they were crushed with a glass rod. The stopper and neck of the bottles were dipped in melted paraffin to make them perfectly water-tight and were then shaken in a thermostat, usually for 48 hours. A sample of the solution was then drawn through a filter of glass wool into a weighed specimen tube and analyzed. The residue was removed and dried on filter paper. Both solvents are very volatile and there was some evaporation as the salts were dried between filter papers. This tended to contaminate the residues with salts from the solution, so that the composition of the residues could not be determined with the same accuracy as the solutions.

---

[1] *Z. anorg. Chem.*, 52, 9, 152; 53, 26; 54, 89.

[2] *Atti. accad. Lincei*, [5] 16, I, 403; *Gaz. chim. ital.*, 39, I, 361.

[3] Foote and Levy, *Am. Chem. J.*, 35, 236 (1906).

Both solutions and residues were analyzed by precipitating mercury as sulphide from hydrochloric acid solution, filtering on a Gooch crucible, and drying at 110–120°. The filtrate was evaporated to dryness and the alkali determined as chloride. Alcohol or acetone crystallizing with the double salts was determined by difference except when otherwise stated. In the mixtures containing sodium and mercuric chlorides, the residues were not analyzed but their composition was calculated. This could be done with sufficient accuracy, since the composition of the solution and of the original mixture were known.

The following results were obtained:

TABLE I.—SOLUBILITY OF SODIUM AND MERCURIC CHLORIDES IN ABSOLUTE ALCOHOL AT 25°.

No	Per cent NaCl in solution.	Per cent. $HgCl_2$ in solution.	Per cent. $HgCl_2$ in residue	Residue contains
1	3.05	47.25	98.17	NaCl and $HgCl_2$.
2	2.90	47.11	70.11	
3	3.09	46.19	12.16	

TABLE II.—SOLUBILITY OF POTASSIUM AND MERCURIC CHLORIDES IN ABSOLUTE ALCOHOL AT 25°.

No.	Per cent. KCl in solution.	Per cent $HgCl_2$ in solution.	Per cent. KCl in residue.	Per cent. $HgCl_2$ in residue.	Per cent. alcohol in residue.	Residue contains
1	0.21	33.69	.....	95.60	....	$HgCl_2$ and $5KCl.6HgCl_2.2C_2H_6O$
2	0.28	33.80	.....	82.03	....	
3	0.22	24.84	17.63	78.00	4.37	$5KCl.6HgCl_2.2C_2H_6O$
4	0.28	6.21	18.27	77.29	4.44	
5	0.25	1.65	.....	73.24	....	$5KCl.6HgCl_2.2C_2H_6O$ and *KCl
6	0.17	1.57	.....	66.21	....	
7	0.38	1.03	.....	4.20	....	

TABLE III.—SOLUBILITY OF POTASSIUM AND MERCURIC CHLORIDES IN ACETONE AT 25°.

No.	Per cent. KCl in solution	Per cent. $HgCl_2$ in solution	Per cent. KCl in residue.	Per cent $HgCl_2$ in residue.	Per cent. acetone in residue.	Residue contains
1	1.29	61.87	. ..	96.37	...	$HgCl_2$ and $KCl.5HgCl_2.C_3H_6O$
2	1.25	61.88	....	94.29	. .	
3	1.39	60.68	4.74	89.85	5.41	$KCl\ 5HgCl_2.C_3H_6O$
4	2.33	56.59	5.01	90.28	4.71	
5	2.58	55.85	5.51	89.75	4.74	
Calculated for $KCl.5HgCl_2.C_3H_6O$			5.02	91.08	3 90	
6	2.77	54.48	....	87.44		$KCl.5HgCl_2.C_3H_6O$ and $5KCl.6HgCl_2.2C_3H_6O$
7	2.79	54.35	. .	83.87		
8	2.93	48.13	15.91	80.16	3.93	$5KCl.6HgCl_2.2C_3H_6O$
9	2.82	38.94	15.90	79.50	4.60	
10	2.51	18 04	17.25	78.00	4.75	
11	3.34	13.26	19.40	76.34	4.26	
Calculated for $5KCl.6HgCl_2.2C_3H_6O$			19.64	76.87	5 47	
12	2.91	10.93	...	67.04	...	$5KCl.6HgCl_2.2C_3H_6O$ and KCl
13	2.99	11.37	....	28.68		
14	2.87	10 66	..	9.14		

In the tables just given, a series of two or more results showing constant solubility and varying residue indicates a mixture of two salts, while variable solubility and constant composition of the residue show the presence of a pure double salt. Referring to Table I, it will be seen that the solubility of the mixtures remains practically constant, showing that the same solid phases are present in every case. The residues vary in composition from nearly pure mercuric chloride to sodium chloride containing only twelve per cent. of mercuric chloride, so that no double salt can be present and the residues consist of varying proportions of the single salts. This conclusion will perhaps be clearer if the results are considered in another way. If a double salt were present, the residue in No. 1 would consist of a mixture of the double salt and mercuric chloride, and No. 3 would consist of the double salt and sodium chloride. As different solids are present in the two cases, the solubilities would be different. The fact that this is not the case shows that the same solids are present. These can only be the single salts, as the composition of the residue varies between such extreme limits.

Sodium and mercuric chlorides therefore do not form any double salt at 25° from absolute alcohol. From water, the salt $NaCl.HgCl_2.2H_2O$ forms. The conclusion appears justified that the water of crystallization is essential to the formation of the double salt, and if the water were removed from the double salt it is to be expected that the residue at 25° would consist of an uncombined mixture of the single salts.

The results in Table II show that one double salt of potassium and mercuric chlorides forms from absolute alcohol at 25°. This salt forms under wide conditions. It was present in pure condition in Nos. 3 and 4 of the table, where the solubility varies. Nos. 1 and 2 consist of a mixture of the double salt and mercuric chloride and Nos. 5–7 of a mixture of the double salts and potassium chloride. The double salt appears to be of an unusual type. A sample was prepared by dissolving mercuric and potassium chlorides in hot alcohol in such proportions that only three or four grams crystallized from about 300 grams of alcohol containing but a small percentage of mercuric chloride. The hot solution was placed in the thermostat at 25° and deposited a mass of silky needles of the double salt. They appeared pure under the microscope. The solution, after standing in contact with the double salt, contained 6.8 per cent. of mercuric chloride, also showing that the pure double salt was present. The salt was removed from the mother liquor, dried very rapidly between filter paper, and analyzed. Alcohol was determined directly by Penfield's method for water. The results, with those previously obtained (Nos. 3 and 4, Table II), are given in Table IV, also the calculated composition of two assumed double salts.

TABLE IV.—RESULTS OF THE ANALYSES OF THE DOUBLE SALT FORMING FROM ALCOHOL.

No.	KCl.	$HgCl_2$	Alcohol.
3	17.63	78.00	4.37 (Diff.)
4	18.27	77.29	4.44 (Diff.)
(Crystallization)	17.07	77.82	4.76 = 99.65
Calculated for $5KCl.6HgCl_2.2C_2H_6O$	17.84	77.76	4.40
Calculated for $3KCl.3HgCl_2.1C_2H_6O$	20.67	75.08	4.25

The three analyses agree among themselves as closely as could be expected, considering that they were all formed under different conditions. The results agree with the formula $5KCl.6HgCl_2.2C_2H_6O$, which is a new type of salt so far as known. The results are so different from the calculated composition of the simpler 3 : 3 : 1 salt that it appears necessary to accept the more complicated formula.

The results, using acetone as solvent, are in Table III. A pure double salt was present in Nos. 3–5 and another in Nos. 8–11. The first corresponds fairly well with the 1 : 5 : 1, the calculated composition of which is given in the table. The results showing the composition of the second salt (Nos. 8–11) vary considerably, as would be expected from the wide variation in the composition of the solutions from which the salt formed. Acetone is much more volatile than alcohol and evaporates so fast that the residues were considerably contaminated with salts from the solution. No. 11 should be the purest sample, as it formed from a solution containing the smallest amount of dissolved salts. It agrees fairly well with the calculated composition of the 5 : 6 : 2 salt, which forms also from alcohol. The salt can be recrystallized. Mercuric chloride and potassium chloride were therefore dissolved in hot acetone in the proportion in which they are present in the 5 : 6 : 2 salt and the solution was allowed to crystallize at 25°. The analytical results were:

	Found.	Calculated for $5KCl\ 6HgCl_2.2C_3H_6O$.
$HgCl_2$	77.52	76.87
KCl	17.46	17.64
C_3H_6O	5.02 (Diff.)	5.47

Acetone is lost rapidly by both salts in the air, so this constituent varies considerably from the calculated values in most of the analyses.

The salts with potassium chloride obtained from the three solvents are summarized in the following table:

From water.	From alcohol.	From acetone.
....	....	$KCl.5HgCl_2.C_3H_6O$
$KCl.2HgCl_2.2H_2O$	....	......
....	$5KCl.6HgCl_2.2C_3H_6O$	$5KCl.6HgCl_2.2C_3H_6O$
$KCl.HgCl_2.H_2O$	....	....
$2KCl.HgCl_2.H_2O$	....	....

It will be noticed that none of the types of salts formed from water are formed from the other solvents, and further, that the 1 : 5 : 1 salt from acetone is not formed either from water or from alcohol. The 1 : 5 salt without water has, however, been prepared with rubidium and with caesium.

From the results obtained in this investigation the conclusion may be drawn that when a double salt is formed containing the solvent, the latter is an essential constituent of the salt and is as important in determining the type of double salt formed, as are the individual salts. The substitution of one solvent for another may even prevent a double salt from forming.

SHEFFIELD CHEMICAL LABORATORY,
NEW HAVEN, CONN.

ADDITIONAL NOTES ON THE ALKALI AND ALKALI EARTH AMALGAMS.

BY G. McP. SMITH AND H. C. BENNETT.

Received March 8, 1910.

The problem as to the nature of the solid amalgams was first systematically investigated by Kerp,[1] who carried out exact solubility determinations with certain members of the class. In every case the solid as well as the saturated solution in equilibrium with it was analyzed.

---

[1] *Z. anorg. Chem.*, 17, 284 (1898).

In a second paper,[1] by Kerp and Böttger, the solubility determinations were continued, and the results were interpreted according to the phase rule. The various phenomena which are possible are discussed at length by Kerp and Böttger. By determining for various temperatures the composition of each of the phases in equilibrium, Kerp and Böttger were in a position to judge whether the solid phase, owing to its constant composition at different temperatures, was to be classed as a chemical individual, and, if so, between what temperatures it was capable of existence.

An undoubted disadvantage of Kerp and Böttger's method lies in the fact that it is extremely difficult to completely separate the crystalline amalgams from the adhering mother liquor, which renders the analytical results for the solid phases very uncertain.[2] For example, the work of Maey,[3] which is free from this error, has rendered the existence of the compound $NaHg_6$, described by Kerp and Böttger, very uncertain.

In our work on the electrolytic preparation of the alkali and alkali earth amalgams,[4] in which large quantities of the solid amalgams were at our disposal, the crystals left behind on filtration showed in several instances a higher alkali content than was obtained by Kerp and Böttger. We therefore repeated their work, at the ordinary temperature, with the addition that the mother liquor left behind on filtration was removed as far as was possible, without undue risk of oxidation, by means of a high-speed electric centrifugal machine. We have included caesium amalgam, which Kerp and Böttger did not prepare, and have also in certain cases repeated their solubility determinations.

Unless otherwise stated, the solid amalgams, obtained by filtration through chamois skin on the filter pump, were introduced into narrow glass tubes (internal diameter = 8 mm.), in which they were melted; while in this condition, the ends of the tubes were vigorously tapped upon the desk, in order to jar to the surface the air bubbles and any hydroxide which might be present. The tubes were then sealed off just above the surface of the melt. They were later cut into 3-centimeter sections, and the amalgams were removed in the form of compact, crystalline sticks, which were centrifuged at high speed for 5–10 minutes in open Gooch crucibles, without filters. Samples weighing 1–8 grams, from which the outer, slightly tarnished surfaces had been removed with a knife, were then at once analyzed. The samples were covered with water (to which a few drops of methyl orange were added), 0.1 *N* hydrochloric acid was run in just to neutral reaction, an excess was then added, and, after the decomposition of the amalgam, this was titrated back with 0.1 *N* sodium hydroxide. The water had acquired its alkalinity, which was generally equivalent to about 1 cc. of 0.1 *N* acid, from the oxidation products present; its action on the amalgam itself was negligible. The alkali content of an amalgam was therefore calculated from the volume of acid that was required to actually decompose the amalgam.

---

[1] *Z. anorg. Chem.*, 25, 1 (1900).

[2] Cf. Kerp and Böttger, *Loc. cit.*, p. 8; also Abegg's "Handbuch," Vol II, part 2, p. 573.

[3] *Z. physik. Chem.*, 29, 119 (1899).

[4] THIS JOURNAL, 31, 799 (1909).

Caesium amalgam, in the form of crystalline sticks, was rapidly oxidized in the centrifuge. Large crystals, obtained by allowing the liquid amalgam, saturated at the ordinary temperature, to stand for several hours in cracked ice, were, however, centrifuged at high speed for 5 minutes without apparent oxidation. Two samples, weighing 7–8 grams, gave, on analysis, 5.05 and 5.07 per cent. of caesium. This was the highest caesium content we obtained. In the cases of sodium and lithium amalgams the crystalline sticks remained compact throughout the treatment, and the results are considered reliable. On disintegrating the solid sticks of the centrifuged sodium amalgam, fine, needle-like crystals of a splendent metallic luster were obtained. To the eye they showed no sign of oxidation, and, unlike those of caesium, rubidium and potassium amalgams, they were clean-cut and free from any indication of mother-liquor. The results for the crystalline amalgams are given as a whole in Table I:

TABLE I.

Amalgam.	Alkali content of crystals separated by filtration		Alkali content of centrifuged crystals	Nearest theoretical formulas	Alkali content required by the foregoing formulas
	Kerp and Böttger	Smith and Bennett.			
Caesium...		4.72	5.05–5.07	$CsHg_{13}$	4.86
				$CsHg_{12}$	5.25
Rubidium.	3.56–3.80	3.55	3.48–3.53	$RbHg_{11}$	3.74
				$RbHg_{12}$	3.44
Potassium.	1.55	1.70	1.63–1.64	KHg_{11}	1.75
				KHg_{12}	1.60
Sodium ..	(0°–40°) 1.76	..	I. 2.28–2.28	$NaHg_6$	1.88
	(42°–100°) 1.96–2.15	...	II. 2.12–2.13	$NaHg_5$	2.25
			I. 1.09–1.09	$LiHg_5$	0.70
Lithium[1]..	(0°–100°) 0.70	0.875		$LiHg_4$	0.87
			II. 1.10–1.11	$LiHg_3$	1.15
Barium....	4.60–4.95	.....	5.38–5.55	$BaHg_{13}$	5.02
				$BaHg_{12}$	5.41
Strontium..	3.33–3.42	.....	3.33–3.53	$SrHg_{13}$	3.25
				$SrHg_{12}$	3.52

[1] Kerp and Böttger had very little crystalline lithium amalgam to work with, which necessarily increased the difficulty of separating the mother liquor by filtration on the filter pump. Their low result is evidently due to the presence of mother liquor.

From the last three columns in the table it is seen that, in spite of the disadvantages of the method, the results tend to indicate the existence of compounds of the formulas $CsHg_{12}$, $RbHg_{12}$, KHg_{12}, $NaHg_5$, $LiHg_3$, $BaHg_{12}$ and $SrHg_{12}$. Nevertheless, the numerical results are misleading, and the only indications which are to be regarded as reliable are those for the sodium and lithium compounds. In the other cases the results prove only that, in the general formula $MeHg_n$, the maximum value of n is 12. It is curious that, in the case of lithium amalgam, Kerp and Böttger, by filtration, obtained values in agreement with the formula $LiHg_5$, while we, by filtration, arrived at the formula $LiHg_4$, and by means of the centrifuge at the formula $LiHg_3$. From his work Maey[1] deduced the existence of $LiHg_5$, of $LiHg_3$ and of other compounds richer in lithium. His results, however, do not so unmistakably indicate the existence of $LiHg_5$, as they do that of $LiHg_3$.

Kerp,[1] in his original paper, did not observe the compound $NaHg_6$, and Kerp and Böttger account for this on the assumption that the compound was decomposed during filtration by the pressure that was then exerted upon its surface in order to completely remove the mother liquor. In their common paper[1] they take exception to the work of Maey, which failed to indicate the existence of a compound richer in mercury than $NaHg_5$. Maey[1] determined the specific volumes of amalgams of varying composition, and from the specific-volume curves he deduced the existence of certain definite compounds. Among others, he determined the specific volume of an amalgam containing 1.90 per cent. of sodium ($NaHg_6$ requires 1 88 per cent.) and obtained the value 0 08168. The next amalgam contained 2.63 per cent. of sodium, and for it he obtained the specific volume 0.08545. We have determined the specific volume of an intermediate amalgam, which contained 2.12 per cent. of sodium ($NaHg_5$ requires 2.25 per cent.) and have obtained the value 0.08277. It is evident that the compound $NaHg_5$ could not have resulted from a specifically heavier one through the agency of pressure alone. Neither is it at all likely that the solid sticks of amalgam were heated much above the ordinary temperature in the centrifuge. Our results harmonize with those of Maey in denying the existence, at the ordinary temperature, of a compound of the formula $NaHg_6$.

Table II contains the weight of amalgamated metal that is present in 100 grams of the saturated liquid amalgam. It should be borne in mind however, that these metals are not present in the solution in the free state; they are present in the form of compounds of the general formula $MeHg_n$, dissolved in an excess of mercury.[2] In the table our own determinations are indicated by asterisks. The other values are those of Kerp and Böttger, which are given for the sake of comparison.

---

[1] *Loc. cit.*

[2] Cf. *Z. anorg. Chem.*, 58, 381 (1908).

TABLE II.

t°.	Cs.	Rb.	K.	Na.	Li.	Ba	Sr.	Ca.[1]
0	*1.96	0.92	0.31	0.54	0.04	0.15	0.73	......
18	*2.61	....	....	....	....	0.32	1.04	....
19.5	....	*1.21	....	....	....	....	..	....
20	....	0.47 *0.46	...	....	....	....	...	......
22	....	....	...	0.63	*0.047	....	....	....
23	....	....	....	....	....	....	*1.12	= or > *0.09
24	....	....	....	....	....	*0.32	....	....
25	....	1.37	0.53	0.65	....	0.34	...	....
26	*2.98	....	....	....	....	....	...	......
30	....	....	0.56	0.67	....	0.43	1.27	......
64.5	....	....	....	....	0.10	....	....	......

In conclusion, it is desired to offer an explanation of the well-known fact that, although mercury itself will not adhere to such metals as iron and platinum, even very dilute alkali and alkali-earth amalgams do readily adhere to them. Upon dipping a platinum wire covered with adhering amalgam into dilute hydrochloric acid, the alkali metal is extracted and the resulting mercury does not continue to adhere to the platinum. It has been shown[2] that, in the decomposition of these amalgams with hydrochloric acid, a point is reached at which there is a sudden increase in the surface tension of the amalgams, accompanied by the sudden evolution of a cloud of minute hydrogen bubbles, and by a sudden decrease in the solution pressure of the amalgams. It would appear, therefore, that the adhesion of the amalgams to platinum and to iron is due rather to the inferior cohesion of the amalgams than to any chemical reaction.

URBANA, ILL.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, OF THE COLLEGE OF THE CITY OF NEW YORK.]

SOME NEW DOUBLE ARSENATES.[3]

BY LOUIS J. CURTMAN.

Received March 11, 1910.

The work on double phosphates[4] suggested the preparation of corresponding arsenates, especially as reference to the literature showed that such compounds had not been prepared. The method which was found to yield these salts was similar to that employed in the preparation of the double phosphates, except as regards the acidity of the solution, which in this case was somewhat greater.

---

[1] We were unable to prepare an amalgam containing more than 0.09 per cent. of calcium. It was filtered at 23°, and was entirely liquid.

[2] THIS JOURNAL, 31, 31 (1909).

[3] Presented in abstract before the Boston Meeting of the American Chemical Society, December, 1909.

[4] THIS JOURNAL, 29, 714 and 1194 (1907).

Preparation.—A solution consisting of 100 cc. of 10 per cent. ferric chloride, 50 cc. of hydrochloric acid (sp. gr. 1.2) and 50 cc. of water was heated to 70°. To this was added gradually and with constant stirring a hot solution of diammonium arsenate containing 105 grams in 175 cc. of water. The addition of the arsenate was followed by the formation of a temporary precipitate which, dissolving on stirring, had the effect of weakening the color of the iron solution; the latter became perfectly colorless when nearly the entire quantity of the arsenate had been added. On adding the last few cc., a slight white gelatinous precipitate formed, which, on heating and stirring, increased in amount and at the same time changed to a finely granular form resembling chalk. The mixture was continuously heated with stirring on an asbestos pad until the temperature rose to 100°, after which it was digested on a boiling water bath for one hour and then allowed to stand overnight. The next day the clear, colorless, supernatant liquid was siphoned off and the residual, perfectly white, compact mass washed twice by decantation with an alcoholic solution (1 part 95 per cent. alcohol to 2 parts of water) containing 0.1 per cent. of ammonium chloride, and then finally with alcohol (1–1) till the washings were free of chlorides.[1] The filtrate was acid to litmus and gave strong tests for ammonium and arsenate, showing that an excess of the precipitant had been used; it did not contain any iron.

The precipitate was first allowed to partially dry in the air, then pulverized, and finally dried to constant weight in a water oven. The yield was 12 grams.

Analysis.—The ammonium was determined by direct distillation with caustic soda into a standard acid solution. The arsenic and the iron were determined in another portion by the following procedure: About one gram of the material was dissolved in 10–15 cc. of conc. hydrochloric acid; when solution was complete, 50–75 cc. of a strong solution of sulphurous acid were added, the whole transferred to a small pressure bottle, and the latter stoppered and heated in a boiling water bath for one hour. After cooling, the contents of the pressure bottle were transferred to an Erlenmeyer flask and without heating, the arsenic was precipitated with a rapid stream of hydrogen sulphide. The filtrate and washings were at once treated with filtered compressed air to drive out the hydrogen sulphide, evaporated to a small bulk, filtered, and the iron determined gravimetrically as Fe_2O_3, or volumetrically with a standard potassium permanganate solution by the Zimmerman-Rheinhart method. The well washed precipitate of As_2S_3 and S was dissolved in concentrated hydrochloric acid with the addition of potassium chlorate, boiled to expel the excess of chlorine, filtered from the undissolved sulphur into a standard volumetric flask and diluted to the mark. Aliquot portions were then pipetted out, rendered alkaline with ammonia, and the arsenic precipitated in the usual way with magnesia mixture and ultimately weighed in a Gooch crucible as $Mg_2As_2O_7$.

---

[1] The final washings, though free of chlorides, gave a test for AsO_4.

	Found.		Theory for $(NH_4)H_2AsO_4$ $FeAsO_4$.
NH_4	4.71	4.66	5.08
Fe	15.45	15.63	15.81
As	42.12	42.06	42.37

Properties of $NH_4H_2AsO_4.FeAsO_4$.—The double arsenate of ferric iron and ammonium is a white powder possessing a faint greenish-yellow tint. It readily dissolves in cold conc. hydrochloric acid with the formation of a yellow solution; it is also soluble in hot nitric and in hot dilute sulphuric acids. Arsenic acid containing 75 per cent. arsenic pentoxide readily dissolves it on heating, yielding a colorless solution from which ammonia, even when added in excess, failed to reprecipitate the arsenate, but instead gave a reddish brown solution, the color of which varied with the amount of double salt originally dissolved. It is insoluble in 50 per cent. acetic acid, also in a strong solution of ammonium chloride. Caustic alkalies completely hydrolyze the compound, the final product being ferric hydroxide; hot water has a similar effect, only to a smaller degree. Hot strong ammonia dissolves the double salt with the formation of a deep red solution. On gentle ignition the double arsenate decomposes, giving off ammonia and water.

Action of Water.—As the chief characteristic of the corresponding double phosphates is their readiness to undergo hydrolysis when washed excessively with water,[1] it was thought worth while to determine whether or not this was the case with the double arsenate and thus explain the difficulty of obtaining a product of a high degree of purity. Accordingly, about two grams of the analyzed salt were treated in a bottle of two liters capacity with 1500 cc. of water at the laboratory temperature, repeatedly shaken, and finally allowed to stand overnight. The next day nearly all the material had settled to the bottom; a very small portion, however; remained in suspension in the colloidal form, which could not be removed by the usual process of filtration. As standing for three days did not cause the colloidal material to settle, recourse was finally had to a porcelain filter operated by strong suction; this proved effective. The residual solid material after the water treatment was noticeably yellow, thus indicating hydrolysis. It was returned to the bottle and treated again with 1500 cc. of water, shaken, allowed to stand overnight, and filtered. The residue which was dried over sulphuric acid possessed a light brown color. Analysis of the clear concentrated aqueous extract showed the presence of AsO_4 and ammonium, but contained no iron. Analysis of dried brown residue after the two treatments with water gave: NH_4, 2.27; Fe, 19.24; As, 31 11.

---

[1] THIS JOURNAL, 29, 717. "Ueber die Phosphate des Kupfers," Doctor's Dissertation, Halle, 1890.

Comparison of these figures with those obtained for the normal salt shows that the action of water on the salt consists in dissolving out arsenic acid and ammonium, accompanied by a change in color of the compound due to the formation of ferric hydroxide. The action is one of *hydrolysis*, precisely similar to that observed with the corresponding phosphates.

Action of Ammonia.—The solubility of the double salt in ammonia suggested the possibility of the formation of basic double arsenate of ferric iron and ammonium similar to that prepared from the corresponding double phosphate. A small quantity of freshly prepared double ammonium ferric arsenate was treated in an Erlenmeyer flask with concentrated ammonia and the mixture heated on a boiling water bath; the white precipitate first became yellow, then brown, and finally, on further heating, dissolved completely to a beautiful reddish brown solution. On adding 95 per cent. alcohol to this solution, a curdy, reddish brown precipitate settled to the bottom and was at once filtered from the overlying cloudy liquid. A portion of the reddish brown material, nearly completely dried in the air, was treated with water; it entirely dissolved to a yellow solution. The ammoniacal filtrate containing an excess of alcohol possessed a very pale yellow color and gave a strong test for arsenic acid with silver nitrate after neutralization of the ammonia with acetic acid. Another portion was evaporated to dryness, taken up with hydrochloric acid and tested for iron. The slight tests obtained indicated that the filtrate contained only traces of iron. Qualitative analysis of the dried precipitate obtained with alcohol showed the presence of iron, arsenic, and ammonium, but the amount was too small for a quantitative analysis. Its qualitative analysis taken, together with its physical properties, namely, color and solubility in water, strongly suggest the corresponding phosphate which forms under the same condition. This will be further investigated.

When dipotassium arsenate was used in place of the ammonium compound, under the same conditions which were found favorable for the formation of the double arsenate of iron and ammonium, a white precipitate was obtained. The result of a qualitative analysis of this substance indicates the existence of the corresponding double alkali arsenate. This compound, together with the double arsenates of aluminium and chromium, are under investigation at the present time.

Summary.

If to a hot ferric chloride solution, strongly acid with hydrochloric acid, diammonium arsenate solution be added to incipient precipitation, and the mixture heated, there forms a white, finely divided precipitate, which analysis showed to be a double arsenate of ammonium and iron of the formula $NH_4H_2AsO_4.FeAsO_4$. Like the corresponding phosphate prepared by the author, the double arsenate readily hydrolyzes when washed with water. It readily dissolves in mineral acids, but is practically insoluble in 50 per cent. acetic acid. Ammonia dissolved it on heating to a deep reddish brown solution, from which 95 per cent. alcohol precipitates a basic double ammonium ferric arsenate. When potassium arsenate was used under the same conditions, a precipitate was obtained which, from the results of a qualitative analysis, appears to be the corresponding double alkali arsenate.

NEW YORK CITY, February, 1910.

A STUDY OF THE PHENOLSULPHONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.

[SECOND PAPER.]

THE COMPOSITION OF THE YELLOW COMPOUND.

BY E. M CHAMOT AND D. S. PRATT

Received February 22, 1910

In our first paper[1] we discussed the composition of the various sulphonic acid reagents which have been suggested for use in this method[2] and showed that the standard phenolsulphonic acid generally used in the United States (Method Am. Pub. Health Association)[3] made by heating a mixture of 15 grams of phenol and 128 cc. of concentrated sulphuric acid for six hours in a flask immersed in boiling water, consists of phenoldisulphonic acid 1-2-4, with always small but appreciable quantities of phenolmonosulphonic acid (para) and a large excess of sulphuric acid. It was also stated that the yellow color obtained by treating a nitrate-containing water residue with this reagent, diluting and making alkaline, was not due, as had long been taken for granted, to salts of picric acid,[2],[3] nor could it be due to salts of mononitro phenols, as believed by Hazen and Clark,[4] nor to salts of dinitro phenols as Montanari supposed.[5]

It had already been shown by Andrews[6] that the mononitro and dinitro phenols are removed from acid solutions by shaking with benzene and that they may be removed from the solvent by shaking with water containing a small amount of alkali, yielding a yellow liquid. Andrews further showed that the nitrophenolmonosulphonic acids are insoluble in benzene and may thus be separated and differentiated from the nitro phenols. Making use of this method, Andrews concluded that mononitro and dinitro phenols and picric acid must be absent from the reaction product of phenolsulphonic acid on nitrates, and therefore assumed that the yellow color must be due to nitrophenolsulphonic acid salts; but as he apparently believed that the reagent consists of monopara acid,[1] one gathers from his paper that he believed the yellow compound to be a salt of the nitromonopara acid. This assumption as to the composition of the reagent and reaction product did not appear to be at all conclusive to the authors, who believed it very necessary to definitely determine the character and structure of the yellow compound by actual isolation and analysis, thus obtaining conclusive proof as to its nature.

---

[1] THIS JOURNAL, 31, 922.

[2] Sprengel, *Pogg. Ann.*, 121, 188 (1863); Grandval and Lajoux, *Compt. rend.*, 62, 101 (1885); Kekulé, *Lehrbuch*, III, 236; Fox, *Tech. Quart.*, 1, 54 (1887); Rideal, *Chem. News*, 60, 261 (1889); Pagnoul, *J. Soc. Chem. Ind.*, 23, 135 (1904); Smith, *Analyst*, 10, 199 (1885).

[3] Gill, THIS JOURNAL, 16, 122 (1894).

[4] Hazen and Clark, *J. Anal. Appl. Chem.*, 5, 301 (1891).

[5] Montanari, *Gazz. chim. Ital.*, 22, I, 87 (1902).

[6] Andrews, THIS JOURNAL, 26, 388 (1904).

As stated in our first paper, it was found early in the investigation that when the cold reagent is poured upon cold residues (the usual method of procedure) no trace ot nitro phenols nor of picric acid could be detected in the reaction products when dealing with such amounts of nitrate as are usually met with in water analysis, 0 to 30 parts per million of nitrogen as nitrate. When, however, the amount approaches 50 parts per million, traces, but only traces of picric acid, appear and may be detected by microchemical analysis.

When either the reagent or the water residue is hot, or when the residue is heated after adding the reagent to it, different results are met with and under these conditions even 5 parts of nitrogen as nitrate may then give slight traces of picric acid, the amount increasing according to the heat treatment, but never reaching more than appreciable traces. The monoparasulphonic acid present is also nitrated by this heat treatment. The presence of these exceedingly small amounts of picric acid was proved by extracting with benzene a large number of water residues after treatment with phenolsulphonic acid, evaporating the solvent and subjecting the extracted material to microchemical tests. Picric acid could not, however, be detected unless a large number of water residues were extracted and hence this compound cannot legitimately be regarded as a product of the reaction as the method is carried out in practice.

In order to obtain the compound yielding the yellow color in alkaline solution, it was decided to isolate it from actual natural water residues containing nitrogen as nitrate. This source of material was adopted in order that there could be no question as to the reactions in the standard method, the authors believing that the pouring of the reagent on pure nitrate residues and the subsequent isolation therefrom of a yellow-colored salt might possibly be regarded as no proof of the products of the reactions obtained in practice.

---

[1] Since the preparation of this article, Lombard (*Bull. soc. chim.*, 6, 1092 (1909)) advances the theory based upon the work of Obermiller on phenolsulphonic acids, that the reagent consists chiefly of orthophenolsulphonic acid and paraphenolsulphonic acid and that the yellow compound consists of about 2 parts of alkali salts of orthonitro phenol and 3 parts of orthonitrophenolsulphonic acid. No details are [illegible] ver, to substantiate this conjecture, which is erroneous

Several thousand residues were obtained by evaporating to dryness, on a water bath, 100 cc. portions of a natural water containing about 10 parts per million of nitrogen as nitrates. These residues were then separately treated in the cold with 2 cc. each of the standard phenolsulphonic acid and the resulting products united. From this acid liquid no color-giving material could be extracted by benzene.

Experiments on a small scale demonstrated that it was possible to separate the yellow-colored salt from the other products present in the alkaline solution by fractional crystallization, and that the potassium salts were best suited for this procedure. Potassium was chosen as the base for several reasons. The reagent always contains a large excess of sulphuric acid and it is evident that the major portion of the products formed must be inorganic sulphates. It is therefore advantageous to have this of a low solubility and as easily crystallizable as possible, hence, potassium is more to be desired than either sodium or ammonium, any one of these three being used in the method. Moreover, potassium is better adapted to quantitative determination.

For the above reasons the acid liquid resulting from the combined residues was carefully neutralized with just sufficient potassium hydroxide solution to develop the maximum color, care being taken to avoid, as far as possible, a marked rise in temperature. The resulting solution was alkaline to litmus This yellow alkaline liquid was then subjected to fractional crystallization in the usual manner, by evaporation, pouring off mother-liquors and combining similar fractions. In another portion of the alkaline liquid fractional precipitation by means of alcohol was resorted to. In both cases potassium sulphate first separated, always, however, stained yellow. The yellow compound, being far more soluble, accumulated in the end fractions. It was soon evident that the compound under investigation was much more soluble in hot than in cold water. After the isolation and purification of the yellow salt, solubility determinations showed that 100 parts of water dissolve 28.8 parts at 40°, 100 parts of water dissolve 19.4 parts at 20° C. The solubility of potassium sulphate, on the contrary, is but slightly increased by a rise of temperature.[1] The fractionations were therefore carried on in warm solutions, making use for this purpose of a large incubator regulated for 40° in our bacteriological laboratory. No attempt was made to ascertain the most suitable temperature for fractioning, since 40° proved remarkably efficient and satisfactory, and this incubator temperature was available.

---

[1] Hazen [illegible] J. prakt. Chem., 29, 471.
Montanari, [illegible] water at 20° C. dissolve 11.11 parts K_2SO_4
Andrews, THIS [illegible] ater at 40° C. dissolve 14.76 parts K_2SO_4

Inasmuch as the reagent consists of phenoldisulphonic acid 1–2–4, together with a small amount of phenolparasulphonic acid, the possible products of the reaction are the normal and acid salts of the two nitrosulphonic acids, the unnitrated sulphonates, mononitro phenols, dinitro phenols, picric acid and dinitro phenolmonosulphonates. Of these compounds the unnitrated sulphonates are colorless, but the nitro compounds are all more or less yellow in alkaline solution.

Both Andrews, by his solubility method, and the authors, by microchemical analysis, have shown that mononitro phenols, dinitro phenols and picric acid are not products of the reaction. The authors have further shown[1] that under the usual method of procedure no nitro group is introduced into the parasulphonic acid. This leaves as the possible compounds formed, the alkali salts of nitrophenoldisulphonic acid and dinitrophenolmonosulphonic acid, the latter resulting from the replacement of one sulphonic acid group by a nitro group—such a reaction, in the cold and with such small amounts of nitric acids as are met with in water analysis, is, however, very improbable, theoretically. Moreover, no evidence of such a compound could be obtained by the authors in any of the material studied. By elimination there remains only the alkali salt of nitrophenoldisulphonic acid.

Nevertheless, as the fractionation proceeded, there separated what appeared to be two nitro compounds. Eventually this was found to be erroneous, one of these being a salt of phenoldisulphonic acid which in crystallizing always occludes relatively large amounts of the nitrosulphonate, thus acquiring shades of yellow, from which it can be completely freed only with great difficulty. Instead, however, of being the tripotassium salt as we assumed at first, because of the presence of a slight excess of potassium hydroxide, it proved, upon isolation and analysis, to be the dipotassium salt of this acid, $C_6H_3OH(SO_3K)_2.H_2O$. This salt is colorless when pure, crystallizing in highly refractive orthorhombic prisms, exhibiting exceptionally strong double refraction (Fig. 1). It cannot therefore be confused in microchemical examinations with the salt of the nitro acid.

The other yellow salt separating was fractioned to free it from potassium sulphate, until its solution failed to yield a turbidity with barium chloride. It was then recrystallized from water at room temperature.

---

[1] Chamot and Pratt, *Loc. cit.*

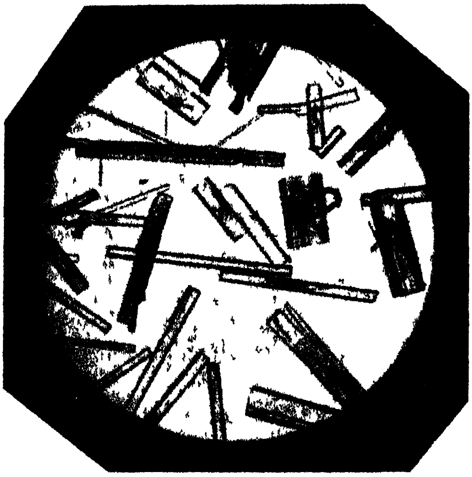


Fig 1 —Dipotassium phenoldisulphonate × 15

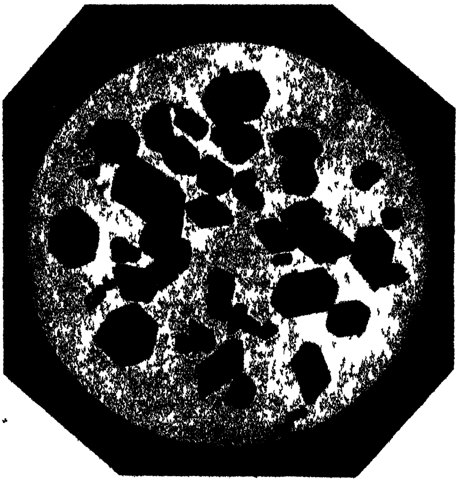


Fig 2 —Tripotassium nitrophenoldisulphonate × 15.

There was thus obtained between one and two grams of a beautifully crystalline, very brilliant, highly refractive orange-yellow salt.

Dry air passed over these crystals caused a loss of water of crystallization, as did heating to 100°. In attempting to dry to constant weight in air it was found that a gradual increase of weight took place, probably due to oxidation. To avoid this, a small electric resistance furnace was designed in which the heating could be done in an atmosphere of carbon dioxide under reduced pressure. This apparatus consisted of a short piece of Jena glass combustion tube wound with nickel wire and surrounded with asbestos-magnesia pipe covering. The temperature could be easily and accurately regulated by a resistance lamp-board and the material contained in platinum boats was readily accessible. The tube was partially exhausted by means of a Chapman filter pump and pure dry carbon dioxide was passed through to remove the moisture liberated. A temperature of 200° was found to be most convenient for removing the water of crystallization. Above 240° the compound turns brown and decomposes without melting. A determination of the melting point of the compound is therefore impossible.

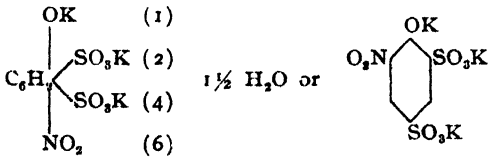
The air-dried, orange-yellow salt gave, upon heating as above described, a loss of weight corresponding to one and one-half molecules of water o crystallization.

Found: 6.16; 5.97; 6.45; 6.47; 6.09; average 6.22 per cent.
Theory for $C_6H_2OK.(SO_3K)_2.NO_2.1\frac{1}{2}H_2O$, 6.13 per cent.

The analysis of the anhydrous salt gave the following results:

	Per cent found			Theory for $C_6H_2OK\,(SO_3K)_2\,NO_2$.
K....	28.46	28.35	28.43	28.37
N....	3.43	3.45	...	3.37
SO_4	46.25	46.21	...	46.47

The salt therefore has the following formula:



$$C_6H_2\begin{cases}OK & (1)\\ SO_3K & (2)\\ SO_3K & (4)\\ NO_2 & (6)\end{cases}\; 1\frac{1}{2}\,H_2O \text{ or}$$

Potassium was determined as the chloroplatinate in the usual manner on the salt direct.

Nitrogen was determined by the Kjeldahl method after first reducing by boiling with zinc dust in a slightly acidulated solution.

For the determination of the sulphonic acid radical the material was first oxidized by several treatments with fuming nitric acid (sp. gr. 1.52) and subsequent precipitation with barium chloride,

This tripotassium nitrophenoldisulphonate crystallizes from aqueous solutions in beautiful orange-yellow, triclinic, many-sided prisms of high refractive index (Fig. 2).

Through the kindness of Professor A. C. Gill, of the Department of Mineralogy and Petrography, the following crystallographic note is given:

"The yellow salt occurs in stout prisms or tabular triclinic crystals. Most of the crystals were too small to measure, but one of the tabular ones, about 0 5 mm. in length, gave fairly good reflections on the goniometer. The plane angle of the large face was a little less than 70°. Each of the edges of the plate is formed by a pair of long, narrow faces. The angles from the top plate to the bottom over one pair are 70° 40′, 64° 25′, and 44° 55′, while over the other pair the angles are 52° 49′, 64° 47′, and 62° 24′. The prismatic habitus as shown in the photograph is much more common than the tubular habitus of the crystal measured.

"The crystals show pleochroism from orange- to sulphur-yellow, are strongly double refracting, and have marked dispersion both of the optic axes and axes of elasticity."

The anhydrous salt is quite a little darker orange in color than the hydrated, and when hot is a cherry-red, retaining its orange color upon cooling. In dilute solutions it is clear yellow but tends towards red as the concentration is increased. With ferric chloride solution it gives a violet-red. Acids added to its solution do not decolorize it, but simply weaken the tint, accounting for the yellow color always obtained in acid solution when a residue high in nitrates is treated with standard sulphonic acid.

A small amount of the dipotassium phenolsulphonate present in the fractions usually greatly modifies the crystal form of the tripotassium nitrophenoldisulphonate, and there may then appear, on rapid crystallization, blade-like crystals pointed at each end or sheaves or clusters of these crystals. It is these modified crystals which confused us for some time, as stated above.

The last fractions of a series always contain as an impurity the very soluble potassium salt of the monoparasulphonic acid, a small amount of this acid being always present in the standard reagent. This salt crystallizes in exceedingly slender and delicate hair-like tufts.

To determine whether the same product is always obtained when the amount of nitrogen as nitrate ranges between the usual limits present in water a special series of water residues was examined. These differed by increments of about two parts of nitrogen per million between the limits of 2 and 30. Each residue was treated with 2 cc. of the standard reagent, diluted and made alkaline with potassium hydroxide. In every case, by microchemical analysis, the yellow color was found to be due to tripotassium nitrophenoldisulphonate. A residue containing 60 parts nitrogen per million gave similar results.

In a third paper the authors will discuss the phenolsulphonic acid method as applied in practice with special reference to sources of error.

Summary.

The yellow color of alkaline solutions of nitrate containing water residues treated with standard phenolsulphonic acid reagent is due to the tripotassium salt of nitrophenoldisulphonic acid, this salt having been isolated and its properties studied.

No other compound giving a yellow color with alkalies could be isolated or detected in appreciable amount, in treated water residues containing from less than .1 to 60 parts per million of nitrogen as nitrate.

In water residues containing over 50 parts per million nitrogen as nitrates traces of picric acid detectable by microchemical methods may be formed in the cold, but traces only.

Water residues heated in contact with phenoldisulphonic acid yield traces of picric acid, but only traces, unless the heating is long continued and the quantity of nitrate high, when appreciable amounts of picric acid may be formed.

Alkali salts of phenoldisulphonic acid occlude sufficiently large amounts of the alkali salts of nitrophenoldisulphonic acid to so color them and so modify their crystal form as to simulate in appearance and behavior another nitro compound.

CORNELL UNIVERSITY CHEMICAL LABORATORY.

[CONTRIBUTION FROM THE LABORATORY OF DR. HERBERT M. HILL, BUFFALO, N. Y.]

THE MERCURY CATHODE IN RAPID ELECTROANALYSIS.

BY W. S KIMLEY.

Received October 8, 1909.

Mercury is superior to platinum for a cathode in several electroanalytical determinations; in some others there is no decided choice, and in several others there is no substitute for the platinum cathode. Some metals can be determined by using a mercury cathode, in an electrolyte that would not give a quantitative deposit on platinum in that the metal seems to be withdrawn from the solvent action of the electrolyte to a certain extent, *e. g.*, copper may be deposited from a solution containing 10 per cent. of nitric acid to within 0.05 per cent. by use of a mercury cathode, while with platinum it would be difficult to recover over 98–99 per cent. With some other metals mercury is superior because it will amalgamate with metals that would not always adhere well to platinum.

The method of H. Filippo,[1] in which the method of Kollock and Smith is modified to obviate working with small volumes, is to place an accurately weighed quantity of mercury in a round-bottomed flask, into the bottom of which is fused a platinum wire which barely projects through the glass and makes connection with the mercury.

---

[1] Leiden Univ., *Chem. Weekblad*, 6, 2269.

When the electrolysis is finished the amalgam is washed with water and alcohol and is poured into a weighing bottle half filled with alcohol. The alcohol is then removed with a pipette and a strip of blotting paper and the mercury is dried and weighed.

This method is open to criticism for several reasons. First, the end of the wire would closely hold a small drop of the amalgam and give low results. Second, although clean mercury can be easily transferred from one dish to another without loss, it would be difficult with many of the amalgams. Mercury loses some of its physical properties when it is alloyed with other metals. The meniscus loses its characteristic convex shape and even becomes concave in some instances.

The following method, originated by the author, is easy of accurate manipulation and will give satisfactory results with those metals to which the mercury cathode is adapted, and it also avoids working with the small volume used by Kollock and Smith. A platinum wire is sealed into the bottom of a round-bottomed fat flask weighing about 25 grams and holding about 125 cc.; 40 grams of mercury will cover the bottom of the flask and the outfit will weigh about 65 grams. When the deposition is complete the solution is siphoned off as far as possible without breaking the circuit, the flask filled with distilled water, and this repeated until the current drops nearly to zero. The flask is then removed from the stirrer and the liquid removed by a glass tube drawn out to a point like the tip of a wash-bottle, and attached to the suction pipe of a filter pump by a rubber tube. When the liquid is nearly all out, the flask is slightly tipped and a bare spot will appear where the tip can be placed against the glass and the last drop of water removed. By this method over 98.5 per cent. of the liquid can be easily withdrawn. After thoroughly washing with water, wash three times with alcohol, removing it in the same way except that it is caught in an empty wash-bottle and distilled over quicklime, when a sufficient quantity has accumulated. The amalgam is then washed once with ether and dried in a hot water oven until there is no odor of ether or alcohol, the flask being removed at intervals of one minute and the vapor blown out.

When it is easy to keep the volume small a convenient cell for the electrolysis can be easily made by placing the mercury in a common straight-sided weighing bottle holding about 60 cc. and making the connection by a platinum wire sealed in a glass tube reaching to the bottom and bent at the top so it nearly touches about half way up (Fig. 1). This keeps the tube at one side of the dish so that it does not interfere with the stirrer. The amalgam is washed and dried as before. In making the tube for connecting with the mercury, the wire is sealed in one end of the tube and the tube is then bent into shape and the other end is sealed so that no moisture may gather in the tube.

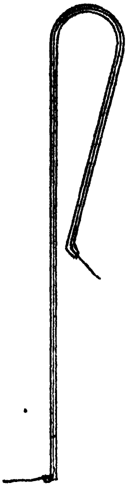


Fig 1.

In using the above cells they should be washed and dried the same before electrolysis as after, to obtain two weights under the same conditions.

The method of connecting with the mercury cathode through the glass tube is not considered superior to sealing a wire in the bottom of the weighing bottle, but it is easily prepared and avoids breaking an expensive piece of apparatus in some subsequent heating or cooling. The same method might be conveniently adapted to connect with the mercury in the round-bottomed cathode chamber (Fig. 2).

Because some of the metals exert a certain influence on others when they are present together, the following experiments were made on the determination of mixtures made by weighing out portions of chemically pure metals and dissolving them together.

A mixture containing, copper 85, lead 5, zinc 5, and tin 5 per cent., was dissolved in nitric acid (sp. gr. 1 20), evaporated nearly dry, diluted with water, boiled, allowed to stand a few minutes, and the precipitate, containing the tin and small amounts of copper and lead, was filtered off and fused with equal parts of sodium carbonate and sulphur in a small covered porcelain crucible. The fused mass was then dissolved in hot water and enough sodium sulphite added to reduce the polysulphides and so render the copper and lead sulphides insoluble. The tin in solution was filtered off and the insoluble sulphides dissolved in nitric acid and returned to the first filtrate, which measured less than 100 cc. This was then placed in the first described cathode chamber, previously prepared and weighed. The anode was of the disc form and was also weighed before attaching to the rotator. The anode was run very slowly to avoid detaching any of the lead peroxide. After starting the rotator the current was turned on and 15 cc. of nitric acid added. The lead separated on the anode and after washing with water, alcohol, and ether, was dried for 1.5 hours at 190° and weighed as peroxide.

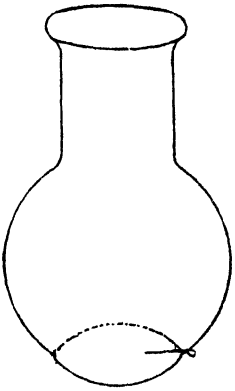


Fig. 2.

The copper separated and formed an amalgam, and after washing and drying the gain in weight of the cathode chamber gave the weight of the copper.

The solution and washings from the determination of lead and copper were run into a casserole, 0.5 cc. of sulphuric acid added and evaporated to fumes to drive off the nitric acid. The residue was then dissolved in a small amount of water and a few drops of sulphuric acid, if necessary. The acid was then neutralized with ammonia and an excess of 0.2 cc. of sulphuric acid added, then placed in the mercury cathode chamber made from the weighing bottle and electrolyzed for zinc. To the solution containing the tin was added 5 cc. of strong sodium hydroxide, 10 cc. of concentrated sodium sulphide solution and 20 grams of ammonium sulphate. It was then digested on the water bath for an hour and the tin deposited, using a platinum dish as a cathode, small amounts of ammonium sulphide being added as necessary to keep the sulphides in solution.

The accompanying table gives some of the results:

Constituent.	Voltage.	Amperes.	Time. Min.	Amount of metal present. Per cent.	Amount of metal found Per cent.	Per cent error.
Copper	5	2	120	85.00	84.98	—0.02
Lead	5	2	120	5.00	5.04	+0.04
Zinc	10	2	90	5.00	5.00	0.00
Tin	6½	2½	120	5.00	4.97	—0.03
				Total,	99.99	
Copper	5	2½	120	85.00	84.97	—0.03
Lead	5	2½	120	5.00	5.03	+0.03
Zinc	10	2	45	5.00	5.01	—0.01
Tin	6½	2½	180	5.00	4.97	—0.03
				Total,	99.98	

In the two following experiments the copper was deposited on platinum foil, other conditions remaining the same.

In the first one, 15.82 per cent. of copper was precipitated on the foil in 120 min., leaving 69.18 per cent. of copper not recovered, and in the second one 18.09 per cent. of copper was precipitated in 150 min., leaving 66.91 per cent. not recovered.

The solutions containing the remainder of the copper were each neutralized with ammonia, made just slightly acid with nitric acid and 0.2 cc. of sulphuric acid added, and the rest of the copper was recovered to within an error of 0.03 per cent. in the first and 0.07 per cent. in the second.

The above does not show that mercury is superior to platinum for the determination of copper, but it indicates that it is better when copper must be determined from a strongly acid solution, as is the case when the separation from lead is made; otherwise the gauze or foil is handier, as it is easier to wash and dry.

To illustrate the working of the process, the results of the analysis of two commercial alloys are given. The copper and zinc were deposited in mercury, the copper in the cathode chamber made from the round-bottomed flask and the zinc in one made from a straight-sided bottle. The results in No. 1 were checked by another chemist who got practically the same results, and in the case of the zinc exactly the same.

	No. 1. Per cent	No. 2. Per cent.
Copper	81.18	83.72
Lead	4.76	5.34
Zinc.	10.04	8.61
Tin	3.40	2.43
Iron	0.63	
	100.01	100.10

It has been stated by Price, *Journal of the Society of Chemical Industry*, that a mercury cathode gives low results with zinc on account of small particles of the amalgam being detached and lost during the process of washing, but by the above method of washing and drying there is apparently no loss, as in nearly every determination on known amounts of zinc the weight of the amalgam indicates at least the whole amount of zinc and in many instances from one- to three-tenths of a milligram more, which is probably due to a slight oxidation of the zinc while drying. Zinc is one of the metals that is best determined as an amalgam, for when deposited on platinum it is difficult to remove without rendering the platinum black and spongy.

Trials with antimony were unsuccessful, as the antimony formed on the surface of the mercury as a black powder and some became lost in washing.

Tin in solution as sulphate forms an amalgam but as yet has given low results.

Several mixtures were made by dissolving copper 0.50, lead 0.35, zinc 0.10 and tin 0.05 gram, and analyzed the same as before, except that the bulk of the lead was precipitated as sulphate and filtered on a Gooch and weighed as sulphate. The small amount remaining was electrolyzed and weighed as lead peroxide and the two added together. This has been found by numerous experiments to give the best results when dealing with comparatively large amounts of lead, as if all the lead is deposited as peroxide the results will be high.

In these mixtures of metals the largest percentage error was 0.04 per cent.

The above described mercury cathode chambers have been placed in the hands of inexperienced persons for the determination of copper, nickel, and zinc, and after a few trials they have been able to get results equally as accurate as the ones recorded above.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 176.]

THE VOLUMETRIC DETERMINATION OF CERIUM IN CERITE AND MONAZITE.

BY F J METZGER AND M HEIDELBERGER

Received March 16, 1910

In a previous number of THIS JOURNAL[1] it was shown by one of us that cerium could be accurately and rapidly determined in the presence of other rare earths by oxidation of the sulphate in sulphuric acid solution with sodium bismuthate, reduction of the ceric salt with an excess of ferrous sulphate, and titration of the excess of ferrous sulphate with potassium permanganate. This method has now been applied with excellent results to the analysis of cerite and monazite sands, and has also been used, with certain modifications, for the determination of cerium in mantle ash, in connection with a colorimetric method for the latter now being worked out in this laboratory. The results on mantle ash are withheld until the completion of this method.

The solutions required for the determination of cerium in cerite and monazite are: (1) A potassium permanganate solution, approximately *N*/40. It was found necessary to standardize this solution at least every two weeks, as it deteriorated slowly in spite of all precautions, presumably owing to the extent of dilution. (2) A solution containing 10 grams of Mohr's salt and 50 cc. of concentrated sulphuric acid per liter. This solution should be standardized every time it is used. The value of the permanganate in terms of iron, multiplied by 3.08415, gives its value in terms of CeO_2 (1910 at. wts.).

In the case of the cerite, 0.5 gram of the finely powdered mineral was fused with potassium bisulphate, and the melt dissolved in about 350 cc. of cold water acidulated with not more than 5 cc. of concentrated sulphuric acid. Care must be taken, in making the fusion, not to allow a ring of finely divided, undecomposed cerite to form on the side of the crucible around the top of the fused mass, otherwise fusion of the residue may be necessary. The solution must also be left in contact with the residue overnight, or until all basic salts which may have formed are dissolved.[2]

The monazites (0.6 gram samples) were decomposed in the usual manner, by heating on a hot plate in small porcelain dishes with concentrated sulphuric acid for at least six hours, the mixtures being stirred occasionally. They were then carefully poured into about 350 cc. of ice-cold water and allowed to stand overnight, or until all basic salts had dissolved.

---

[1] THIS JOURNAL, 31, 523.

[2] When these conditions have been carefully followed, further treatment of the residue is unnecessary.

The cerite and monazite solutions were then filtered, heated to boiling, and the rare earths precipitated by the addition of a large excess (100 cc. or more) of a saturated solution of oxalic acid. After standing overnight, the precipitated oxalates were filtered off and washed with a 1 per cent. solution of oxalic acid. It had been expected that the sulphuric acid solution of the sample could be treated directly wth sodium bismuthate without removal of impurities, but the separation of the rare earths as oxalates was found necessary owing to the discovery that manganese interfered, giving high results. Experiments now under way in this laboratory indicate that the manganese is held in solution apparently in the quadrivalent form, and a volumetric method for its determination is now being worked out.

Three general methods suggested themselves for the treatment of the oxalate precipitate:

1. It may be washed off the filter paper with water, dissolved with 20 cc. of concentrated sulphuric acid, and, after the addition of 5 grams of ammonium sulphate and dilution to 100 cc., oxidized by means of 2 grams of sodium bismuthate. This method was successfully used in analysis 5*a*, but could not be applied to 1, as it was found in one case that enough basic salts were precipitated to hold back some cerium, while in another case an excessive amount of bismuthate had to be used, resulting in a very heavy precipitation of basic salts. While this method cannot, in general, be recommended, it is believed that it will give satisfactory results when the precipitate of oxalates is small, and care is taken to avoid the introduction of organic matter from the filter paper, preferably by the use of hardened papers.

2. The precipitate and paper may be transferred to a platinum crucible and ignited, finally with a blast lamp. The mixed oxides are then warmed in the crucible for several hours with 10 cc. of concentrated sulphuric acid, allowed to cool, and carefully poured into about 100 cc. of cold water. It was found that incomplete solution results, even on long standing, but on the addition of 10 cc. more of concentrated sulphuric acid, and subsequent evaporation on a hot plate, a clear, yellow solution is obtained. This is diluted to 100 cc., 2 grams of ammonium sulphate added, and oxidation effected by means of 1 gram of sodium bismuthate. This method was used with good results in analysis 9.

3. The oxalates may be washed off the filter with hot water and converted to hydroxides by boiling with sodium hydroxide. The precipitate is filtered off, washed well with hot water, and dissolved through the filter by means of dilute sulphuric acid. The filtrate is diluted to 100 cc. after adding enough sulphuric acid to bring the amount up to 20 grams of the concentrated acid. Ammonium sulphate and sodium bismuthate are then added as in method 2. Method 3 was used for

all the analyses except those mentioned above. While not as rapid as method 1, it was found to be entirely trustworthy, and in addition proved itself far more convenient and rapid than 2. It is therefore recommended as the best of the three methods.

In all the determinations, after adding the sodium bismuthate, the solution was slowly brought to the boiling point, allowed to settle a moment, and then decanted from the residue through a gooch. The residue must be thoroughly washed with 2 per cent. sulphuric acid in order to remove all the cerium. The filtrate is then titrated with the ferrous sulphate solution until an excess has been run in, the excess being titrated back with the permanganate solution.

Duplicate determinations were made on each sample with the following results:

No.	Material.	Source.	Per cent CeO_2.
1a	Cerite	Unknown	22.08
1b			21.97
2a	Monazite	Brazil	28.60
2b			28.74
3a	Monazite	Brazil	22.84
3b			22.56
4a	Monazite	Brazil	23.13
4b			23.16
5a	Monazite	Brazil	23.93
5b			24.01
6a	Monazite	Brazil	27.25
6b			27.09
7a	Monazite	Brazil	24.31
7b			24.28
8a	Monazite	North Carolina	22.19
8b			21.99
9a	Monazite	North Carolina	22.54
9b			22.49
10a	Monazite	North Carolina	20.47
10b			20.55

The above results show that the new volumetric method for cerium yields accurate results when applied to monazite and cerite. In addition to its accuracy, the method recommends itself on account of its ease of manipulation and its rapidity.

QUANTITATIVE LABORATORY.

THE REACTION BETWEEN HYDRIODIC ACID AND BROMIC ACID IN THE PRESENCE OF A LARGE AMOUNT OF HYDROCHLORIC ACID.

BY D. L. RANDALL.

Received March 11, 1910.

Andrews[1] has shown that when a solution of potassium iodide, strongly acidified with hydrochloric acid, is titrated with a standard solution of potassium iodate the reaction takes place according to the following equation:

---

[1] THIS JOURNAL, 25, 756.

$$2KI + KIO_3 + 6HCl = 3KCl + 3ICl + 3H_2O$$

When a small amount of chloroform is present the completion of the reaction can be very easily recognized by the fading of the violet color in the chloroform and the amount of iodide present accurately determined from the quantity of iodate used. Andrews also used this method for the determination o' free iodine, chlorates, chromates, arsenites and ferrous salts.

At the summer meeting of the American Chemical Society, at Detroit, it was mentioned that very few uses were now made of bromates, in spite of the fact that the salts of bromic acid can easily be made in a condition of great purity. It seemed possible that potassium bromate might be substituted for the more expensive potassium iodate for the determination of the iodides and the other substances worked upon by Andrews.

Experiments were made in which standard potassium bromate solution was added to potassium iodide in a solution that contained about fifty per cent. of strong hydrochloric acid, and it was soon found that a less amount of potassium bromate solution was used than that required by the equation

$$2KI + KBrO_3 + 6HCl = 3KCl + 3H_2O + 2ICl + BrCl.$$

The amount of bromate used was almost exactly two-thirds the quantity required by the above equation. That seemed to indicate that three molecules of potassium iodide instead of two were oxidized by one molecule of bromate, so that the reaction probably goes as follows:

$$3KI + KBrO_3 + 6HCl = 4KCl + 3H_2O + 2ICl + IBr.$$

That the bromate and iodide act in this way is shown by the experiments in which the following solutions were used:

1. A standard solution of potassium bromate made by dissolving 5.5673 grams of the recrystallized salt in one liter of water.
2. An approximately tenth-normal solution of potassium iodide prepared by dissolving 16.607 grams of the commercial C. P. salt in a liter of water.
3. An approximately tenth-normal solution of sodium thiosulphate.

The sodium thiosulphate solution was standardized by treating a known amount of the standard bromate solution with two grams of potassium iodide and five cc. of concentrated hydrochloric acid and titrating the iodine set free with the thiosulphate. The strength of the potassium iodide solution was determined by treating 20 cc. of the iodide solution in a distilling flask with an excess of ferric alum and 5 cc. of sulphuric acid (1 : 1) and distilling over the iodine set free into potassium iodide solution and titrating with the thiosulphate.

In each of the following experiments 20 cc. of the potassium iodide solution in a 250 cc. glass-stoppered bottle were treated with different amounts of hydrochloric acid and five cc. of chloroform. The bromate solution was run in until, after violent shaking, the chloroform had lost its pink color. The results obtained are given in the following table:

A.

KI soln cc	HCl (1 . 1) cc	H_2O cc	$KBrO_3$ soln cc.	I taken. Gram.	I found. Gram	Error.
20	40	0	19.92	0.2523	0.2530	+0.0007
20	30	10	19.94	0.2523	0.2532	+0.0009
20	20	20	20.00	0.2523	0.2539	+0.0016

B.[1]

KI soln cc	Conc HCl. cc	H_2O. cc	$KBrO_3$ soln. cc	I taken Gram.	I found. Gram	Error.
20	40	0	19.87	0.2508	0.2523	+0.0015
20	40	0	19.87	0.2508	0.2523	+0.0015
20	40	0	19.81	0.2508	0.2516	+0.0008
20	20	20	19.87	0.2508	0.2523	+0.0015
20	30	10	19.90	0.2508	0.2527	+0.0019
20	40	0	19.80	0.2508	0.2514	+0.0006
20	40	0	19.85	0.2508	0.2521	+0.0013
20	40	0	19.80	0.2508	0.2514	+0.0006

In all cases a slight positive error could be observed, probably due to the fact that the end point was less sharp with the iodine and chloroform than with the starch iodine indicator.

If a bromide is substituted for an iodide, while a reaction takes place and the chloroform is colored, still complete bleaching is not obtained even by adding an excess of the bromate, so we cannot determine in this way what reaction takes place between bromides and bromates in the presence of strong hydrochloric acid. With ferrous salts there is no coloration of the chloroform at all.

Summary.

This work has shown that like the iodate the bromate will oxidize the iodide, but the bromate is a more powerful oxidizer in that the bromine itself will react with one atom of iodine. Further, iodides may be easily and rapidly determined by titrating the iodide solution with standard bromate solution in the presence of twice its volume of hydrochloric acid.

New Hampshire College, Durham, N. H.,
March 1, 1910.

COMPOSITION OF SEA WATERS NEAR BEAUFORT, NORTH CAROLINA.

By Alvin S. Wheeler.

Received February 25, 1910.

Clarke, in his "Data of Geochemistry," reports no analyses of sea waters along the coasts of North America. Possibly no careful analyses have been made. These analyses were undertaken owing to the increasing interest which biologists are taking in the chemical composition of sea water as a feature of the environment of sea life. The work was done during the summer of 1909 at the U. S. Biological Laboratory at Beaufort, North Carolina, and for the U. S. Bureau of Fisheries. I wish to express here my thanks to the Commissioner of Fisheries, Mr. George M. Bowers, for his courtesy in permitting the publication of my report.

---

[1] Solutions of different strengths than those used in A were taken.

Sodium and Potassium.—The most careful investigation of sea water was made by Dittmar, reported in the "Report of the Scientific Results of the Exploring Voyage of H. M. S. Challenger, 1873–1876," Vol. I, Physics and Chemistry. This work was not at hand when this investigation was undertaken and the usual methods for determining sodium and potassium were adopted These are given in "Mineral Waters of the United States," *Bull.* 91, Bureau of Chemistry, by J. H. Haywood and B. H. Smith. The determination of sodium came out low, the total bases being insufficient for the total acids. This experience is in agreement with the statement of Dittmar that "the routine method adopted in mineral salt analysis, *i. e.*, the elimination of lime and magnesia and subsequent joint determination of soda and potash as sulphates or muriates, would never give sufficiently precise results." My determinations were therefore corrected by employing Dittmar's method of "total sulphates." Ten cubic centimeters of water were weighed out in a glass-stoppered weighing bottle and evaporated to dryness in a platinum dish with a small excess of sulphuric acid, a dilute solution of known strength being employed. After evaporation to dryness over steam, the residue was heated on a sand bath and finally ignited to dull redness to constant weight. The following figures show the value of the method. The values for sodium sulphate by the total sulphate method and by calculation from the determinations of the other constituents differed by two parts in a thousand. On the other hand, the values obtained experimentally, after elimination of sulphuric acid, lime and magnesia, and by calculation from the determinations of the other constituents, differed anywhere from thirteen to thirty in a thousand.

Calcium and Magnesium.—Forty cubic centimeters of water were weighed out and transferred to a beaker. One cc. 5 *N* hydrochloric acid was added and the mixture boiled to expel carbon dioxide. After cooling, four cc. 5 *N* ammonium hydroxide and five cc. *N*/2 ammonium oxalate solution were added. The next day the supernatant liquid was decanted upon a filter, the residue redissolved in dilute hydrochloric acid and reprecipitated with ammonium hydroxide and a little ammonium oxalate solution. The following day the calcium oxalate was filtered upon the filter already used, washed with hot water and ignited in a platinum crucible to constant weight. The combined filtrates were concentrated to a volume of 150 cc., cooled, mixed with ten cc. normal disodium phosphate solution and ten cc. strong ammonium hydroxide. The next day the precipitate was filtered off, washed with dilute ammonium hydroxide and finally with water. It was ignited in an open platinum crucible.

Chlorine.—Eight cc. sea water were weighed out and transferred to a beaker. Titration was conducted with a standard solution of silver nitrate (one cc. = 0.003555 gram Cl), using potassium chromate as indicator. In order to better observe the change of tint, a standard of comparison was made by precipitating a sodium chloride solution with excess of silver nitrate and re-establishing the yellow color with a little more salt. The silver nitrate solution was standardized by means of two samples of sodium chloride: 1. A sample labeled "Sodium Chloride, C. P., Eimer and Amend" was dissolved in pure water and reprecipitated with hydrochloric acid. It was filtered off, washed with water, and ignited. 2. A sample labeled "Sodium Chloride, C. P. Special. Baker's Analyzed Chemicals." The impurities were CaO = 0.001 per cent., Fe = 0.0001 per cent., SO_3 = 0.001 per cent.

Sulphuric Acid.—To 25 cc. sea water, which had been weighed, were added, while hot, 2 cc. dilute hydrochloric acid and 3 cc. *N* barium chloride solution. The next day the barium sulphate was filtered off, washed with hot water and ignited in a platinum crucible.

Carbon Dioxide.—The determination of carbon dioxide was carried out by titrating 100 g. of water with 0.05 *N* hydrochloric acid, using phenolphthalein as indicator for normal carbonates and then methyl orange for bicarbonates. The results were checked by titrating with 0.05 *N* acid potassium sulphate as recommended by Cameron.

Specific Gravities.—The specific gravities were determined by the use of a pycnometer of U-form. The temperature employed was that of the laboratory, in order to avoid the unusual condensation of moisture on the pycnometer if lower temperatures were used.

The Waters.—Five samples of water were analyzed. The localities were marked upon a chart of Beaufort Harbor which accompanies my report to the Bureau of Fisheries: *A*. Taken in Beaufort Inlet. *B*. At the laboratory dock where water is taken for the laboratory aquaria. *C*. In Bogue Sound, opposite Moorehead, where *Toxopneustes* are abundant. *D*. At a point between the eastern end of Beaufort and Bird Island shoal. *E*. At Green Rock, in Newport river, near the entrance to Core Creek.

The results are given below in four tables. Comparison is made with Dittmar's results. Challenger water No. 924, a deep sea water, is given in three tables, because this is the only water whose composition is reported in parts per thousand of water. It does not, of course, represent the average. For example, the value for chlorine is 55.396 per cent. of the total salts whereas the average for the 76 analyses is 55.420. Comparison is also made with the analysis of a water mentioned in an article by Curt Herbst in *Archiv fur Entwickelungs mechanik der Organismen*, **5**, 651. This water is from the Mediterranean sea below Naples, Italy.

TABLE I.—PARTS PER 1000 GRAMS OF SEA WATER.

	A	*B*	*C*	*D.*	*E*	924.	Herbst.
Cl ...	19.909	19.635	19.767	19.810	17.571	19.201	21.137
SO_4. .	2.754	2.681	2.699	2.730	2.378	2.673	3.237
CO_3. .	0.132	0.129	0.129	0.129	0.129	0.143	6.080[1]
Na...	11.049	10.968	11.022	11.036	9.771	10.607	11.936
K	0.442	0.390	0.394	0.394	0.368	0.380	0.409
Ca . . .	0.433	0.429	0.440	0.436	0.392	0.483	0.473
Mg	1.353	1.301	1.313	1.323	1.177	1.301	1.362
Total.. .	36.072	35.533	35.767	35.867	31.786	34.788	38.634

TABLE II.—PARTS PER 1000 GRAMS OF SEA WATER.

	A.	*B.*	*C.*	*D*	*E.*	924.	Herbst.
NaCl .	28.043	27.836	27.977	28.006	24.796	26.882	30.292
KCl	0.842	0.742	0.751	0.751	0.702	0.725	0.779
$MgCl_2$. .	3.379	3.245	3.300	3.335	2.972	3.413	3.240
$MgSO_4$ ...	2.417	2.328	2.320	2.372	2.062	1.937	2.638
$CaSO_4$ . .	1.171	1.168	1.202	1.188	1.039	1.591	1.605
$CaCO_3$	0.220	0.214	0.214	0.215	0.215	0.240	0.080[2]
Total.	36.072	35.533	35.767	35.867	31.786	34.788	38.634

TABLE III.—PERCENTAGE OF TOTAL SALTS.

	A.	*B*	*C.*	*D*	*E*	Dittmar[2]	Herbst.
Cl. . .	55.191	55.257	55.270	55.231	55.280	55.292	54.710
SO_4	7.635	7.546	7.547	7.612	7.481	7.692	8.380
CO_3. . .	0.366	0.363	0.361	0.360	0.405	0.207	0.207[3]
Na. ..	30.630	30.867	30.818	30.768	30.741	30.593	30.894
K.. ...	1.226	1.098	1.102	1.099	1.157	1.106	1.059
Ca. . .	1.201	1.208	1.230	1.216	1.233	1.197	1.224
Mg.. ..	3.751	3.661	3.672	3.714	3.703	3.725	3.526
Total .	100 per cent.					Br 0.188	

TABLE IV.—PERCENTAGE OF TOTAL SALTS.

	A.	*B.*	*C.*	*D*	*E.*	924.	Herbst
NaCl .. .	77.743	78.340	78.229	78.083	78.010	77.274	78.408
KCl . . .	2.334	2.088	2.100	2.093	2.208	2.085	2.016
$MgCl_2$.. .	9.367	9.132	9.227	9.300	9.350	9.811	8.386
$MgSO_4$....	6.700	6.551	6.487	6.612	6.487	5.569	6.828
$CaSO_4$.. .	3.246	3.287	3.361	3.313	3.269	4.572	4.154
$CaCO_3$....	0.610	0.602	0.596	0.599	0.676	0.689	0.208[3]
Total....	100 per cent.						

Specific gravities at 28.7° (corr.).

1.0227 1.0222 1.0226 1.0227 1.0193

UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, N. C.

---

[1] The residue insoluble in water after evaporation to dryness.

[2] Average of analyses of 77 Challenger waters.

[3] Insoluble residue.

APPARATUS FOR DRYING FLASKS, ETC.[1]

By Charles Baskerville and Reston Stevenson.

Received February 19, 1910

The frequent requirement in chemical work for dry flasks, bottles, test tubes, cylinders, beakers, etc., suggested the construction of a drying apparatus. Many forms of such an apparatus were devised, made, tried and found unsatisfactory. Then an electrical drier was constructed, about fifteen various forms were tried, and finally the form as presented in this paper was adopted as satisfactory. It is shown in Fig. 1.

The air enters the side tube *A* near the bottom, is heated by the red hot platinum wire *B* at the top of the apparatus, and the hot air which streams out dries the vessel which is placed over the top of the tube.

The air, before entrance, should be dried and cleaned by passing through sulphuric acid, calcium chloride, and cotton wool, so that the flask is dried more quickly and is cleaner than if ordinary air from the laboratory or from pipes were used. Compressed air is the convenient source of the air, but a foot-bellows is sufficient to operate the apparatus.

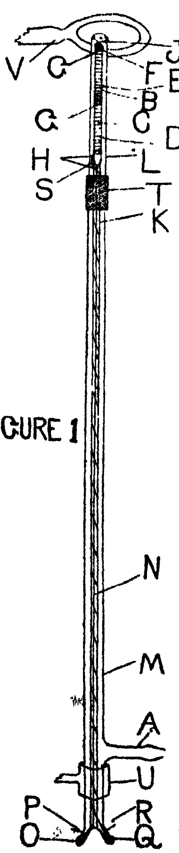


FIGURE 1

The heating is done by means of platinum wire *B*, wound around a porcelain tube *C*. If this platinum wire were the same gauge throughout its entire length, it would be dark at the bottom of the porcelain tube where the air first meets the platinum wire, dull red at the middle of the tube, white-hot at the top of the tube where the air which meets the platinum wire is already heated, and the length of wire which passes back through the center of the porcelain tube away from the air would fuse. This unequal heating, due to the different rates of radiation, can be avoided by constructing the heating wire by winding 10 inches of platinum wire of diameter 0.0115 inch around the lower part of the porcelain tube; 15 inches of diameter 0.013 inch around the middle and upper part of the tube; and 10 inches of diameter 0.14 inch around the top of the tube and back through the opening in the center of the tube. Also the windings are spaced unequally; the wires of diameter 0.0115 and 0.013 are wound closely at the lower part and farther apart at the upper part of the porcelain (see Figs. 1 and 2). In this way there are about 19 turns of diameter 0.0115 inch (see *D*), 25 turns of 0.013 (*E*), and 4 turns of 0.014 (*F*). By this arrangement, during use, the platinum coil glows with nearly uniform brightness throughout its length, so that the maximum efficiency is obtained with minimum weight of wire and minimum length of porcelain tube.

---

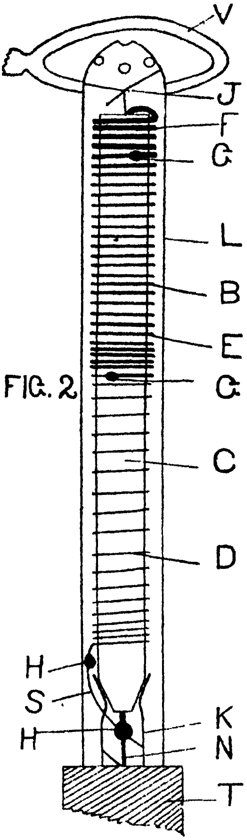
[1] Read before the New York Section, American Chemical Society, Dec. 17, 1909.

The platinum wires are joined to each other autogenously (*G*,*G*) in the flame of the gas-oxygen blast lamp. The platinum wires are joined to the copper wires (*N*,*S*) autogenously in the flame of the air-gas blast lamp. These joints (*H*,*H*) are strong and neat.

The porcelain tube *C* is 2¾ inches long, of diameter 0.15 inch, and has an opening through its center of 0.035 inch diameter. Into the hole at the top enters a platinum wire, *J*, which has at its top 3 radiating platinum wires (the 4 wires are readily joined together at the same point in the flame of the gas-oxygen blast lamp). These wires reach out to the hard glass tube *L* and prevent the red hot platinum wires from touching and cracking the glass tube. The lower end of the porcelain tube is beveled and rests in the flared end of the soft glass tube *K*, which rests upon the bottom of the soft glass tube *M* and supports the porcelain tube.

Through the tube *K* goes the copper wire *N* of diameter 0.02 inch. This wire is sealed into the tube at *O* with blue enamel glass and presents a terminal at *P*. The external portion of the wire is wound around the tube several times in order to prevent breaking at *O*. The other copper wire, *S*, is wound around the glass tube *K*, whereby short-circuiting with wire *N* is prevented. The other terminal is at *R*. These copper wires do not get hot and do not appreciably oxidize.

FIG. 2



The tip *L* is made of hard glass. It can be readily removed from the rest of the apparatus, disengaging it at the rubber tube *T*, so that broken tips can be replaced or other forms of tips can be substituted within a few seconds. The form of tip shown in Figs. 1 and 2 has six small holes at the top, which sprinkle the effluent air in every direction and is the best form for most uses, although various shapes can be made for special purposes.

Between the terminals *P* and *R* there is a resistance of about 5 ohms, and a current of about 6 amperes is requisite to heat the platinum wire to bright redness, so that the apparatus operates with a 30-volt current. In order to cut down a 110-volt current, about 50 cents worth of German silver wire, No. 22, will be sufficient. The entire length of the apparatus is about 30 inches. It is supported by a clamp, *U*, attached to an iron stand. Also attached to this stand is a ring, *V*, which supports the flask over the drier at an adjustible height.

The temperature of the current of air at a distance of an inch from the tip is about 100°.

In the operation of the dryer, the precautions must be taken that in starting, the current of air should be turned on before the current of electricity; and in stopping, the electricity should be turned off before the air.

The advantages of this form of drying apparatus are—

1. The heat is supplied just before the air enters the flask, so that there is no time given for the air to cool off before it reaches the moisture.

2. The air is both hot and dry, and is blown in all directions forcibly against the walls of the vessel which is to be dried, so that the operation is rapid. Furthermore, the temperature is not high enough to produce hysteresis of standard apparatus.

3. There is no necessity for the use of alcohol and ether, and the air which reaches the flask is free from dust, oil, etc., so that the flask is clean when it is dry.

This apparatus has been in practical use several months in the physical chemistry laboratories of the College of the City of New York, for drying bottles, flasks, test tubes, cylinders, beakers, etc., and has been found rapid, effective and convenient. This apparatus, apart from the external resistance, may be ordered from Eimer & Amend, at a cost of about $6.00.

DEPARTMENT OF CHEMISTRY.
COLLEGE OF THE CITY OF NEW YORK.

ANALYSIS OF SOME BOLIVIAN BRONZES.[1]

By MORRIS LOEB AND S. R MOREY

Received February 26, 1910.

Through the kindness of the authorities of the American Museum of Natural History, we were enabled to analyze portions of certain implements collected in the region around Lake Titicaca. It will be seen that these metals differ remarkably in composition, and indicate the possession of considerable metallurgical skill by the inhabitants of that region. The absence of the slightest traces of silver may be taken as a proof that the tin was derived from cassiterite, rather than native tin. The composition of Specimen IV suggests its preparation from domeykite, or some other copper arsenide, fairly free from sulphur. Owing to the small mass of samples, which were drilled or cut from the specimens, the density determinations, made with water in a pycnometer, are only approximate. In Specimen VI the porosity of the material undoubtedly occasioned a low result. Tin and copper were separated by potassium polysulphide, the former determined as stannic oxide and the latter electrolytically. Arsenic was separated from copper by Crookes' method, and sulphur was weighed as barium sulphate after oxidation with nitric acid in a sealed tube.

---

[1] Paper read at the December meeting of the New York Section.

I. Museum No. 1842. Small chisel or pinch-bar, 18 x $1^1/_8$ x $^1/_2$ inches. Very tough. Density, 8.68.

II. Museum No. B-1840. Implement 5-6 inches long, very hard and tough; pale color. Density, 8.94.

III. Museum No. 1959. Thick wide chisel $4^1/_2$ inches long, tough but less hard. Density, 8.92.

IV. Museum No. 1-859. Socketed spear-head, 12 inches long. Density, 8.89.

V. Museum No. 2413 Fragment of pointed bar 6 inches long. Density, 8.61.

VI. Museum No. 1949. Small cast chisel; contained characteristic air-holes or "pipes." Apparently contained considerable *oxide*. Density, 8.18(?).

ANALYSIS.

	I.[1]	II.	III.[1]	IV.	V.[2]	VI.
Cu	91.81	90.51	95.59	97.43	94.96	91.43
Sn.	7.56	8.92	4.48	.	4.98	7.05
Pb	. .	. . .	.	trace(?)		
Fe	trace	trace	trace	trace	. . .	trace
S	.	trace		little	0.53	. .
As.		.		2.14	. .	. .
	99.37	99.43	100.07	99.57	100.47	98.48

To this report may be added the record of an analysis, made in 1901, by Dr. A. E. Hill with one of us, of a figurine found in Honduras. Color, pale yellow; density, 8.94-6. Cu 93.19, Sn 1.64, Pb 1.60, Fe 0.40 per cent.; Au, Sb and Zn absent.

NEW YORK, February, 1910.

[CONTRIBUTIONS FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE FUNDAMENTAL LAW FOR A GENERAL THEORY OF SOLUTIONS.[1]

BY EDWARD W. WASHBURN.

Received March 3, 1910.

Nomenclature.

C	Volume concentration.
(1) C_p, (2) c_p	Molecular heat capacity of (1) a liquid, (2) a gas.

---

[1] Average of two complete analyses.

[2] Average of three concordant analyses.

[1] Presented at the Second Decennial Celebration of Clark University, Worcester, Mass., September 16, 1909.

ΔC_p	Decrease in molecular heat capacity attending a change in state of aggregation.
(1) K_C, (2) K_N	Equilibrium constant in terms of (1) volume concentrations, (2) mol fractions. (Products of the reaction in the denominator.)
K_S	Solubility product in terms of mol fractions.
(1) L_S (2) L_v (3) L_F	Molecular heat of (1) sublimation, (2) vaporization, (3) fusion (under constant external pressure).
(1) N, (2) N'	Mol fraction of (1) solvent, (2) solute.
(1) n, (2) n'	Number of mols of (1) solvent, (2) solute.
p	Gas or vapor pressure.
P	External pressure on a liquid or solid.
Q_π	Heat evolved when the reaction $a\text{A} + b\text{B} + \ldots = m\text{M} + n\text{N} + \ldots$ takes place from left to right in a solution under osmotic equilibrium.
R	Gas constant.
(1) T, (2) T_F, (3) T_O, (4) T_B, (5) T_{Bo}	(1) Absolute temperature, (2) absolute temperature of the freezing point of a solution, (3) of the freezing point of the pure solvent, (4) of the boiling point of a solution, (5) of the boiling point of the pure solvent.
U	Total energy decrease produced when the reaction $a\text{A} + b\text{B} + \ldots = m\text{M} + n\text{N} + \ldots$ takes place from left to right
(1) v, (2) V	Molecular volume of (1) a gas, (2) a liquid.
π	Osmotic pressure.
μ	Thermodynamic potential.
ψ	Fugacity.
ξ	Activity.

I. The Development of the Modern Theory of Solutions.

Upon the foundations laid by the labors of van't Hoff and Arrhenius has arisen the structure which we know to-day as the Modern Theory of Solutions. Before van't Hoff's epoch-making discovery of the thermodynamic relations which bind together the colligative properties[2] of dilute solutions, our knowledge concerning these important quantities was confined to a set of apparently unconnected empirical laws. Van't Hoff's generalization of these laws, followed almost immediately by the Ionic Theory of Arrhenius, stimulated greatly the study of solutions and made possible the rapid development and perfection of our present theory. Investigation has, however, been confined chiefly to the domain of dilute solutions and the Modern Theory of Solutions has remained almost entirely a theory of dilute solutions. The reason for this is, I believe, due largely to one of those historical "accidents" which occur now and then in the development of science. The history of this "accident" and the manner in which it came about forms a chapter in physical chemistry of interest alike to the chemist and to the philosopher.

Perhaps the best way to form a clear idea of the process of evolution of our present theory of solutions is to consider first the colligative properties of solutions and the relations which connect them. These quantities—the osmotic pressure, vapor pressure, freezing point, boiling point, etc.—have played such an important and vital part in the development of our solution theory that a clear idea of their relations to one another is absolutely essential to a proper understanding of the theory and of its development. The nature of these relations is expressed by the following statement: *The colligative properties of a solution are connected by a set of rigorous differential equations which involve no assumptions except the two laws of thermodynamics.* The equations are as follows:

---

[2] Following Ostwald, the term "colligative properties" is used to embrace such properties as osmotic pressure, boiling point raising, freezing point lowering, vapor pressure lowering, etc.

(1) Osmotic Pressure and Freezing Point,

$$d\pi = \left(\frac{-L_F}{V}\right)\frac{dT_F}{T_F}. \qquad (82)$$

(2) Vapor Pressure and Freezing Point,

$$dp = \left(\frac{L_S}{v}\right)\frac{dT_F}{T_F}. \qquad (92)^*$$

(3) Osmotic Pressure and Vapor Pressure,

$$d\pi = \left(\frac{-v}{V}\right)dp. \qquad (77)$$

(4) Osmotic Pressure and Boiling Point,

$$d\pi = \left(\frac{l_v}{V}\right)\frac{dT_B}{T_B}. \qquad (90)$$

To these should be added a number of others, such as the relation between the electromotive force of a concentration cell and either vapor pressure (74) or osmotic pressure (70), and (16 and 14) the mutual relations among the osmotic pressures or vapor pressures of the constituents of a physical mixture or (30 and 30*a*) the substances concerned in a chemical equilibrium, etc.[3] While the following discussion applies with equal force to all of these relations, it will perhaps be conducive to clearness, if we confine our attention chiefly to the four relations given above.

From the method of derivation of these relations, it is clear that they do not involve any assumptions regarding the concentration of the solution, nor do they depend in any way upon the nature of the dissolved solute or its degree of association, dissociation, or solvation. In fact, if one knows, for example, the vapor pressure, freezing point lowering or boiling point raising for a solution of any nonvolatile solute, he has the means of calculating the osmotic pressure for the same temperature without knowing either the concentration of the solution or the nature of the solute. There may be one or several solutes present and they may associate, dissociate, or unite with each other or with the solvent in any manner and to any extent. These questions are in no way involved in the calculation. Since relations such as those existing among the colligative properties of a solution involve only the two laws of thermodynamics, it will be convenient to refer to them as "*purely thermodynamic relations*," to distinguish them from an important group of relations which involve the composition of the solution and the nature of its components, and which we will now proceed to consider.

---

[3] The derivations of these relations and a more detailed discussion of them are given in a previous paper, "A Simple System of Thermodynamic Chemistry Based upon a Modification of the Method of Carnot" (THIS JOURNAL, 32, 467 (1910)). For convenience in reference these equations are given the same number here as in the previous paper where the significance of the quantities appearing in the equations is explained in detail.

Let us consider a solution of any solute A in any solvent B, and let our problem be to express each of the colligative properties of the solution as a function of its composition or its "concentration." This problem can in general be solved only by direct experiment for the particular solvent and solute under consideration. From what has preceded, however, it is evident that as soon as we know the relation between *any one* of the colligative properties and the composition of the solution, the other relations become thereby determined. If, for example, we determined the freezing point of the solution for a series of concentrations, we could calculate thermodynamically the osmotic pressure, the vapor pressure, etc., for the same concentrations and thus derive an equation connecting each of these quantities with the concentration. The colligative property which should be chosen for experimental study in a given case would depend upon the relative ease and accuracy with which the several quantities could be determined and the temperature range which it was desired to cover; also in some cases upon whether the requisite "caloric quantities"[4] were known with sufficient accuracy or could be determined readily.

The relation between any one of the colligative properties and the concentration of the solution for any given solvent and solute will obviously depend upon the degree of association, dissociation and solvation of the solute.[5] Since the magnitude of these effects and their dependence upon the concentration are in general unknown quantities, the problem is too complex for any complete solution. In general, therefore, it is necessary to make a separate investigation for every solvent and solute in order to establish the desired relation connecting some one of the colligative properties with the concentration. To leave the problem in this condition, however, is naturally not very satisfactory, and the course usually followed by science when confronted with a problem which is too complex is first to simplify the problem. Let us try to trace the process of simplification which has been followed by science in the present instance.

Since association or dissociation of either solvent or solute molecules introduces complications, the first step in the process of simplification is obviously to consider the simple case of a solution in which neither takes place. Since the union of a portion or all of the solute molecules with the solvent molecules (solvation) is also a complicating factor, the next step in the process of simplification would naturally be to eliminate this factor also by assuming no solvation. After making these simplifications our problem would read as follows: What are the relations connecting the colligative properties with the composition in the case of a solution in which the number of molecular species present is equal to the number of components?[6] Let us call such a solution, provisionally, an "ideal solution," postponing until later a more definite and accurate description of the properties of the type of solution to which the term "ideal" should be applied.

---

[4] Proposed by van der Waals to distinguish heat capacities, latent heats, heats of reaction, etc., from colligative properties.

[5] It is hardly necessary to remark that this statement tacitly assumes that the desired relation is to be one which involves the number of mols of the solute.

[6] For example, in the case of two components, a solvent and one solute, there would be only two different kinds of molecules; for a solvent and two solutes, only three different kinds of molecules, etc.

There is, however, another method by which the complicating factor of solvation can also be eliminated. Willard Gibbs, in his monumental work on thermodynamic chemistry, has taught us that the proper way to represent the composition of any phase is by the means of the mol fractions of its several components.[7]

Now in the case of a solution, the mol fraction of the solute (for example) will be altered if it becomes solvated on going into solution, owing to the consequent change in the number of solvent molecules. Such a complication can be eliminated from our problem, as explained above, by assuming no solvation; or it can be likewise eliminated *by taking the solution sufficiently dilute.* For, as the solution becomes more and more dilute, the limit approached by the mol fraction of the solute is the same whether solvation occurs or not.[8]

Owing to an "historical accident" the latter method of eliminating the complication of solvation has been the one followed by science, instead of the former and more logical one. The "historical accident"[9] in this instance was van't Hoff's brilliant discovery of the remarkably simple equation connecting osmotic pressure with temperature and concentration in very dilute solutions. Starting with this equation as a basis and using the principles of thermodynamics, he showed us how to construct a complete theory of dilute solutions.

As the field of dilute solutions became more and more developed, both from the experimental and theoretical side, investigators began to turn their attention to the subject of concentrated solutions. Investigation in this direction has usually taken the direction of attempts to extend the osmotic pressure equation by the introduction of quantities corresponding to the *a* and *b* of van der Waals' *condition equation* for gases, upon the basis of kinetic conceptions derived from an assumed analogy between osmotic and gas pressure. Other investigators have sought to attribute all of the deviation of concentrated solutions from the equations of dilute solutions, to solvation, and have even gone so far as to compute on this basis the approximate degree of hydration in some very concentrated aqueous solutions, for example. Still other attempts have been taken in the direction of an extension of our present equations by the addition of a series of terms containing a number of constants intended to express the influence of the solute molecules upon one another and upon the solvent.

---

[7] This system has been consistently followed by all investigators who use systems of thermodynamics based upon Gibbs' thermodynamic potential. The reason that it has not been followed by others is because they have confined themselves to the region of dilute solutions, where it is possible to use one of the limiting forms approached by the mol fraction of the solute, as the concentration approaches zero.

[8] To illustrate, if we put n' mols of a solute in n mols of a solvent and no solvation (or dissociation or association) occurs, then the mol fraction of the solute is $\frac{n'}{(n' + n)}$. If, however, on the average x mols of solvent are combined with each mol of solute, the mol fraction of the (solvated) solute is $\frac{n'}{[n' + n - n'x]}$ or $\frac{n'}{[n'(1-x) + n]}$. As the solution becomes more and more dilute, both expressions approach $\frac{n'}{n}$ as their limit. This is the familiar ratio which appears in our boiling point and freezing point equations. In the case of our osmotic pressure equation, instead of writing it $\pi = \left(\frac{n'}{n}\right)\left(\frac{RT}{V}\right)$, where V is the molecular volume of the solvent, it is customary to substitute $V_s = nV$ and write $\pi V_s = n'RT$. Here again, if the solution is *sufficiently* dilute, it is obviously immaterial whether we understand V_s to mean the volume of the solution or the volume of pure solvent in which the n' mols of solute were dissolved in preparing the solution.

[9] The expression, "historical accident," is, of course, used in the philosophical sense.

Attempts to obtain a satisfactory theory of concentrated solutions in any of these directions give no promise of success. An attempt to "explain" why, as a solution becomes more and more concentrated, it deviates more and more from the equations of very dilute solutions is somewhat analogous to an attempt to explain why the sine of angle, which for sufficiently small angles is equal to the angle, deviates more and more as the angle grows larger. The reason is, of course, a purely mathematical one. Similarly in the case of solutions there is first of all a purely mathematical reason why concentrated solutions should deviate from the equations of the infinitely dilute solution. The equations of dilute solutions are the limiting forms assumed by more general equations, owing to the fact that certain terms become negligible as the concentration approaches zero. In other words we have in our dilute solution laws only a portion, the residue, so to speak, of a more general set of laws for solutions of all concentrations. Consequently before science can hope to make any progress in the region of concentrated solutions she must go back to the point where the simplifying assumption of a dilute solution was unconsciously introduced, and, in place of it, make the simplifying assumption of an "ideal solution" as we have defined it above. We come, therefore, to

2. The Laws of the Ideal Solution.

Owing to the simplicity of the thermodynamic treatment of solutions by what we may call the osmotic-cyclical-process method and the fact that it uses conceptions which are comparatively easy to grasp and processes which can be readily pictured in the mind, it has been the favorite system among physical chemists. The fact that the theories developed by the advocates of this method have been confined almost entirely to the domain of the dilute solution is not due to any inherent fault in the method. In addition to this method we have the systems of thermodynamics based upon the Gibbs thermodynamic potential and its related functions. These systems have been the favorite ones among physicists and those who by training and inclination were accustomed to the use of potential functions, and it is among the advocates of the thermodynamic potential that we find the first successful attempt to formulate a theory of solution which is free from the assumption that the solution must be dilute.

This theory has been developed in Holland by van der Waals and his associates, especially by van Laar. The first attempt was made in 1893 by Hondius Boldingh[10] in an Amsterdam Dissertation which so far as I have been able to learn has never been published elsewhere. In the following year van Laar[11] published two papers in which he derived a set of "exact formulae for osmotic pressure, change in solubility, freezing point, boiling point, etc." His results were expressed in a series of equations in which the concentration of the solution appeared in a term, $\ln(1-N')$, in which N' represents the mol fraction of the solute. The equations contained, in addition, an undetermined function of the molecular thermodynamic potentials of the constituents. In numerous subsequent publications van Laar has advocated with great warmth and zeal, the use of the thermodynamic potential method and the introduction of the concentration of the solution into the equations by means of the expression $\ln(1-N')$, instead of assuming that the solution is dilute. Van Laar has in fact advocated a theory of solution which is entirely free from the assumption that the solution must be dilute. The foundations for this theory have existed in the literature for the last fifteen years. If it occurs to any one to wonder why the theory has not come into general use in the chemical world, he has only to glance through some of van Laar's papers, especially his earlier ones, and the reason will be more or less obvious.

---

[10] Boldingh, "De Afwijkingen van de Wetten voor Verdunde Oplossingen." Dissertation, Amsterdam, 1893.

It is my present purpose to free this theory from the language of the thermodynamic potential and to develop it in the so-called "osmotic language."[12] Stated in this language, our problem is to determine the functional relation between some one of the colligative properties of the solution and its concentration in the case of an ideal solution. Theoretically we can start with any one of the colligative properties we choose, but since our present theory of dilute solutions is usually assumed to start with the osmotic-pressure-concentration relation, it will perhaps be more interesting to develop our theory of the ideal solution from the same standpoint.

Let us, therefore, turn to the equation which expresses the osmotic pressure[13] for a very dilute solution:

$$\pi = \frac{n'RT}{V_s} = \frac{n'RT}{nV} \qquad (100)$$

In this equation, n' is the number of mols of solute in n mols of solvent and V is the molecular volume of the pure liquid solvent. Let us now make use of the method, introduced by Willard Gibbs, of expressing the composition of the solution by means of the equation $N' + N = 1$, where N' is the mol fraction of the solute and N that of the solvent. The above equation can now be written:

$$\pi = \frac{\frac{n'}{n+n'}RT}{\frac{n}{n+n'}V} = \frac{N'RT}{NV} \qquad (101)$$

---

[11] van Laar, *Z. physik. Chem.*, 15, 457 (1894).

[12] The "language of the colligative properties" would be a better term. Too much importance is usually ascribed to osmotic pressure in our solution theory.

[13] Throughout this paper, we shall understand by the term "osmotic pressure," the pressure difference π as defined by the equation $\pi = P - P_A$, where P_A is the pressure upon the pure liquid solvent A when it is in equilibrium (through a membrane or medium permeable only to itself) with the solution under the constant pressure P. This has been discussed more fully in the previous paper (THIS JOURNAL, 32, 478 (1910)).

We have long recognized the fact that our osmotic pressure equation expresses *strictly* only the limit approached by the osmotic pressure as the concentration of the solution approaches zero. Let us therefore write the equation itself so that it will indicate this fact. This gives us

$$\Delta\pi = \left(\frac{\Delta N'}{N}\right)\left(\frac{RT}{V}\right). \tag{102}$$

Seeing the equation in this form it is natural to suspect that the real relation might possibly be

$$d\pi = \left(\frac{dN'}{N}\right)\left(\frac{RT}{V}\right), \tag{103}$$

or since by definition—$dN' = dN$,

$$d\pi = \left(\frac{-RT}{V}\right) d \ln N. \tag{104}$$

Stated in words, this means that not only would the addition of dN' mols of solute to a pure solvent involve an increase (*i. e.*, from 0 to $\Delta\pi$) of osmotic pressure which satisfies equation (104) but that it would also involve the *same* increase in osmotic pressure when added to a solution whose osmotic pressure is π. If such proves to be the case (and we shall see that in many cases, at least, it does), our Modern Theory of Solutions has remained a theory of infinitely dilute solutions, because we have failed to recognize the fact that we have been working with true differential equations, and that in order to obtain the "theory of concentrated solutions" which we have been seeking, the *only thing we needed to do was to integrate our equations.*

In the case of osmotic pressure, for example, if we integrate equation (104), we shall obtain an equation which contains no assumption whatever regarding the concentration. The solution may be infinitely dilute or infinitely concentrated or may have any concentration between these limits. In order to do this we have only to put $V = V_0(1 + \alpha\pi)$, where V_0 is the molecular volume of the pure solvent under the standard pressure P and α is its coefficient of compressibility, and on integration we obtain the Boldingh-van Laar[14] equation for osmotic pressure:

$$\pi + \tfrac{1}{2}\alpha\pi^2 = \left(\frac{-RT}{V_0}\right)\ln(1 - N') \tag{105}$$

---

[14] The history of this equation (105) is very interesting. The differential form as expressed by equation (104) was obtained by van der Waals as early as 1890 (*Z. physik. Chem.*, **5**, 163) but no attempt was made to integrate it, only the case of dilute solutions being discussed, for which case it assumes the form of equation (102) or (100). In 1893 Hondius Boldingh, a student of van der Waals, making use of the thermodynamic potential of Gibbs, derived equation (105) in the following form (Diss., Amsterdam, 1893, p 57):

$$\pi V_0 = -RT \ln(1 - N') + aN'$$

This differs from equation (105) as we have obtained it above, only in the fact that the compressibility of the liquid is neglected and a small correction term aN' is added, a being a quantity which, according to the molecular theory of van der Waals, expresses the mutual influence of the components of the solution upon each other. For "ideal solutions" it is negligible.

Boldingh apparently made no attempt to apply his equation. The same equation was obtained the following year by van Laar (*Loc. cit.*) and in numerous publications

Having come to the conclusion that the integral of equation (104) should represent the osmotic pressure for an "ideal solution," whatever its concentration, we naturally seek for experimental confirmation before adopting it finally.[15] Owing to the great difficulty of making accurate and

---

since then, this investigator has given various derivations of this equation usually by methods involving the thermodynamic potential (cf., however, note 15). In 1897 an osmotic pressure equation in its essential points practically identical with equation (105) was derived by Willard Gibbs (*Nature*, **60**, 461 (1897)) by a method of balanced columns. Finally G. N. Lewis, in a recent paper (THIS JOURNAL, **30**, 675 (1908)), has obtained equation (105) by a derivation involving his "activity" function and based upon the assumption that the "activity" of the solvent is proportional to its mol fraction. Both van Laar (*Proc. Acad. Sci.*, Amsterdam, **9**, 55 (1906)) and Lewis (*Loc. cit.*) have discussed the relation of this equation to the van't Hoff equation and have made comparisons of the values of osmotic pressure given by it with those obtained by Morse and Frazer by direct measurement, in the case of aqueous solutions.

[15] In view of the fact that the van't Hoff equation for osmotic pressure is usually regarded as derivable from the kinetic theory by methods analogous to those used in the kinetic derivation of the perfect gas laws (that is, on the assumption that osmotic pressure is caused by the molecular bombardment of the solute molecules), it may not be without interest to include here a brief kinetic derivation of the differential form of equation (105). For this purpose I shall modify slightly the derivation given by van Laar (*Sechs Vorträge*, p. 20).

Consider two solutions of the same solute in the same solvent, both under the external pressure P and separated from each other by a membrane permeable only to the molecules of the solvent. According to a theorem of Boltzmann, the number of solvent molecules which diffuse per second through a unit surface of the membrane in the two directions is given by the expressions:

(*a*) From the weaker solution to the stronger,

$$n_w = (1 - N'_w)e^{-\frac{\lambda+PV_w}{RT}}. \qquad (107)$$

(*b*) From the stronger solution to the weaker,

$$n_s = (1 - N'_s)e^{-\frac{\lambda+PV_s}{RT}}. \qquad (108)$$

In these equations e is the base of natural logarithms, N'_w and N'_s are the mol fractions of solute in the weaker and the stronger solutions respectively, V is the volume of the solution, R the gas constant, T the absolute temperature and λ a quantity which is a function of the temperature and which depends upon the units of measurement. By adjusting the pressure on the two solutions we can make the number of molecules of solvent which pass in the two directions equal; in other words the two solutions will be in equilibrium as respects the passage of the solvent from one to the other. Under these conditions the right-hand members of the above equations can be placed equal to each other, giving us the equation:

$$(1 - N'_w)e^{-\frac{\lambda+P_wV_w}{RT}} = (1 - N'_s)e^{-\frac{\lambda+P_sV_s}{RT}} \qquad (109)$$

Let us now impose the condition that the "weaker solution" shall be the pure solvent and that the "stronger solution" shall be an infinitely dilute solution in this solvent and shall be under an external pressure P. Under these conditions the above equation assumes the form

$$e^{-\frac{[\lambda+(P+d\pi)V]}{RT}} = (1 - dN')e^{-\frac{(\lambda+PV)}{RT}}. \qquad (110)$$

Dividing through by $e^{-\frac{(\lambda+PV)}{RT}}$ and using the logarithmic instead of the exponential reliable osmotic pressure measurements, it would be an unnecessary waste of time and effort to seek experimental confirmation in this direction, especially as the equation can be tested *just as satisfactorily* by means of its thermodynamic derivatives. Of these we will consider first, the vapor pressure derivative. The thermodynamic relation connecting osmotic pressure and vapor pressure is

nomenclature, we obtain equation (104):

$$d\pi = \left(\frac{-RT}{V}\right) d \ln (1 - N') \qquad (104)$$

After giving a kinetic derivation for equation (105), van Laar follows it with what he terms a "rein thermodynamischer" proof. Such a proof is of course impossible, if by "purely thermodynamic" we are to understand that the equation can be shown to be a necessary consequence of the two laws of thermodynamics and nothing else. In his papers on the subject, van Laar does not distinguish carefully between purely thermodynamic relations and relations which involve additional assumptions. This makes it difficult for the reader, who has not had considerable experience in the use of the thermodynamic potential, to appreciate just what assumptions he is making and what grounds he has for making them. Van Laar also falls into the error of attributing the failure of the modern theory of solutions in the region of concentrated solutions, to an inherent weakness in the osmotic method which he condemns severely, at the same time advocating with great zeal the thermodynamic potential as the *only* quantity which is in a position to completely solve the problem (*Sechs Vorträge*, p. 19). This point of view is absolutely unjustified and is doubtless partially responsible for the fact that the many excellent and valuable features of this investigator's contributions to this problem have not received from the chemical world the consideration which they deserve. Whether we should adopt a system of thermodynamic chemistry based upon the entropy function (as worked out by Horstmann), or upon one of the thermodynamic potentials of Gibbs or Planck, or upon the "fugacity" and "activity" as defined by Lewis or upon the "osmotic pressure" and its related colligative properties, is largely a philosophical question in which the personal equation is an important factor. The "best" system from one point of view is not the "best" from another, and instead of adopting one of these systems and severely condemning the others, we should rather rejoice that the problems of our science are being attacked from these different points of view. All of these systems rest upon the common ground of the first and second laws of thermodynamics and any chemical problem which can be solved in terms of one of them can be solved in terms of all. I cannot therefore agree with van Laar, that the so-called "osmotic" system "läuft auf seinen letzen Beinen" and "nach wenige Jahre wird abgereist sein."

Van Laar also attacks the so-called "gas theory" of solutions, that is, the theory that what we call "osmotic pressure" is a real pressure which exists within an isolated solution due to a molecular bombardment by the solute molecules. On this question, I sympathize largely with van Laar's point of view. His exposition of the difficulties in the way of such a theory is clear and convincing and I shall not, therefore, attempt any further discussion of the question at this time. In this connection, however, it is interesting to recall the views held by Willard Gibbs upon this point. In speaking (*Loc. cit.*) of the osmotic pressure in the case of a solution A, containing a solute, D, he says:

"But we must *not* suppose in any *literal* sense, that this difference of pressure represents the part of the pressure in A which is exerted by the D-molecules, for that would make the total pressure calculable by the law of Boyle and Charles."

$$d\pi = \left(\frac{-v}{V}\right)dp. \qquad (77)$$

Combining this with equation (104) so as to eliminate π we obtain

$$Vdp = RTd\ln N. \qquad (111)$$

If the vapor can be regarded as a perfect gas we can put $v = \frac{RT}{p}$ and obtain

$$d\ln p = d\ln N \qquad (112)$$

which on integration gives

$$p = p_0N \qquad (113)$$

where p_0, the integration constant, is the vapor pressure of the pure solvent. Since the terms solvent and solute are quite arbitrary, we can state therefore in general that the partial vapor pressure of any constituent of an "ideal solution" is proportional to its mol fraction, if the vapor obeys Boyle's law. We have therefore in equation (113) an excellent means of testing our fundamental osmotic equation.

The next question which confronts us is, where are we to look for solutions whose characteristics approach most closely those which we have assumed for our "ideal solution," or in other words where can we find solutions for which we have reason to believe that we know the mol fractions of the constituents in the solution? Our attention is naturally directed towards mixtures of the so-called "normal" liquids of which many examples are to be found among the hydrocarbons of the benzene series and their substitution products. These liquids possess the property of mixing with each other in all proportions, the process of solution being accompanied by little if any heat effects or volume changes, such as would, in general, necessarily occur, if the process of solution were accompanied by chemical reactions such as solvation or changes in the degree of association or dissociation of any of the components. In general the physical properties of these solutions are additive with respect to the constituents. This behavior is, however, just what we should expect in the case of the "ideal solution" which we have assumed. We may therefore expect to find experimental confirmation of our osmotic pressure equation in the case of these solutions. Fortunately data are at hand in the vapor pressure measurements of Zawidski and others. These data show most conclusively that equation (113) expresses the partial vapor pressure for *both* constituents throughout the total concentration range from zero to infinity for some dozen or fifteen different mixtures.[16] Freez-

---

[16] The mixtures which obey this vapor pressure law are as follows:

(1) CO_2—CH_3Cl; (2) C_6H_{14}—C_8H_{18}; (3) $C_2H_4Cl_2$—C_6H_6; (3) $C_2H_4Br_2$—$C_3H_6Br_2$; (2) CH_3OH—C_2H_5OH; (2) $CH_3COOC_2H_5$—$C_2H_5COOC_2H_5$; (2) C_6H_6—$C_6H_5CH_3$; (4) C_6H_6—C_6H_5Cl; (4) C_6H_6—C_6H_5Br; (2) $C_6H_5CH_3$—$C_6H_5C_2H_5$; (4) $C_6H_5CH_3$—C_6H_5Cl; (4) $C_6H_5CH_3$—C_6H_5Br; (2) C_6H_5Cl—C_6H_5Br.

References:

[1] Kuenen, *Z. physik. Chem.*, **11**, 38 (1893).

[2] Young, *J. Chem. Soc.*, **81**, 768; **83**, 68 (1903).

[3] von Zawidski, *Z. physik. Chem.*, **35**, 129 (1900).

[4] Linebarger, This Journal, **17**, 615, 690 (1895).

This experimental confirmation of the theory of the ideal or "perfect" solution was pointed out in a recent paper by G. N. Lewis (*Loc. cit.*) who has computed some ing point data furnish additional confirmation of the correctness of our fundamental equation. Van Laar finds, for example, that the "freezing point" curve for solutions of mercury in tin, throughout its entire range (from $t = 232°$ C., $N' = 0$ to $t = -19°$, $N' = 0.9964$), is satisfactorily represented by an equation which rests on the same basis as our fundamental osmotic pressure equation.

This perfect experimental confirmation, combined with the light which is thrown upon the subject by the historical criticism, constitutes a most convincing array of evidence in favor of the adoption of the Theory of the Ideal Solution, as the best provisional *General Theory of Solution.* Before turning to a more detailed consideration of the equations of the Ideal Solution, let us state clearly the general characteristics of such a solution. They are as follows:

I. The number of molecular species present is equal to the number of components.

II. The physical properties of the solution are connected with the physical properties of its components in the pure state by the equation

$$X = xN + x'N' + x''N'' + \qquad (114)$$

in which X is the molecular property in question (*e. g.*, molecular heat capacity, molecular volume, molecular refraction, molecular internal energy, etc.), x (x', x'', etc.) the molecular property of a constituent in the pure state and N (N', N'', etc.) its mol fraction in the solution.

III. The third and most important characteristic is that which describes the thermodynamic relations. The manner of stating this characteristic depends upon what system of thermodynamics one chooses to make use of. I shall therefore state it in three different "languages."

(*a*) *The Gibbs Thermodynamic Potential System.*—According to van Laar the thermodynamic characteristics of the "ideal solution" are expressed by the equation

$$\mu = \mu_0 + RT \ln N \qquad (115)$$

in which μ is the molecular thermodynamic potential of a constituent in the solution, μ_0 the molecular thermodynamic potential of the same constituent in the pure state and N its mol fraction in the solution.

(*b*) *The Fugacity-Activity System of Lewis.*—Lewis uses a system of thermodynamic chemistry based upon two quantities, the "fugacity" ψ, and the "activity" ξ, whose relation to each other is expressed by the equation

$$\psi = \xi RT \qquad (116)$$

and which are connected with the thermodynamic potential by the equation

$$\mu = C + RT \ln \psi \qquad (117)$$

where C is a function of the temperature only. According to Lewis the "perfect solution" is defined by the equation

$$\xi = \xi_0 N \qquad (118)$$

or what amounts to the same thing,

$$\psi = \psi_0 N. \qquad (119)$$

That van Laar's and Lewis' methods of describing the "ideal" or "perfect" solution are identical is made evident by writing equation (119) in the form

$$RT \ln \psi = RT \ln \psi_0 + RT \ln N, \qquad (120)$$

---

tables which exhibit in a very striking manner the excellent agreement of equation (105) with the experimental data, even in the most concentrated solutions.

and combining it with equation (117) when we obtain at once equation (115).

(*c*) *The Colligative Property System or the So-called Osmotic System.*—According to this system, the relation between the colligative properties of the Ideal Solution and its composition is expressed by a set of equations which is composed of the equation

$$d\pi = \left(\frac{-RT}{V}\right) d\ln N \qquad (104)$$

and its thermodynamic derivatives.[17]

Having established fundamental equations for the Ideal Solution, let us now derive a set of equations for such a solution similar to our present equations for dilute solutions, but free from any assumptions as to the concentration of the solution. In deriving such a set of equations we could start either with our osmotic pressure equation (104) or the vapor pressure derivative (112). In either case we should obtain the same set of equations. There is not much reason for choosing one of these equations rather than the other as a starting point. Each possesses certain advantages for this purpose. In the following derivations, however, I shall start with the osmotic pressure equation (104) in each case. This procedure will allow of direct comparison with our corresponding derivations for dilute solutions and it moreover avoids the necessity of using the gaseous phase in the derivation of a relation which is independent of the properties of the vapor. The procedure for obtaining our set of equations is very simple. In each instance, it consists simply in combining equation (104) with the proper purely thermodynamic relation and then integrating the result. The purely thermodynamic relations have all been obtained by the author in the previous publication[3] to which the reader is referred for their derivation. For convenience in reference these equations will be designated by the same numbers as in the preceding publication. All numbers below 100 refer to the previous paper.

3. Vapor Pressure.

We have already derived this equation for which the integrated form is

$$p = p_0 N \qquad (113)$$

where p is the partial vapor pressure of any molecular species from an ideal solution in which its mol fraction is N, and p_0 is its vapor pressure in the pure liquid state at the same temperature. For a single non-volatile solute whose mol fraction is N' this can also be written in the form

$$\frac{\Delta p}{p_0} = N' = \frac{n'}{(n + n')}. \qquad (121)$$

If in a mixture of say two liquids, polymerization of one or both constituents, or chemical combination between them occurs, we can obviously make use of equation (113) to determine the exact nature and extent of these processes if we know the necessary partial vapor pressure data. Derivatives of equation (113) for special cases of association and of chemical combination have been applied recently with considerable success by Ikeda[18] and by Dolezalek[19] to the elucidation of the chemical condition of several pure liquids and of their mixtures. The accumulation of accurate and reliable vapor pressure data is of the highest importance to a clearer and more complete knowledge of the nature of solutions. For reasons which I have stated elsewhere,[21] the vapor pressure equation is the relation best adapted to serve as a basis for the experimental attack on the problem of concentrated solutions.

---

[17] Regarding the general characteristics of the Ideal Solution as stated above, it should be noted that although *in general* the *absence* of heat effects or volume changes on mixing two liquids may be taken as evidence for the absence of accompanying chemical reactions, the reverse is not necessarily the case. Heat effects and volume changes *may* and doubtless do occur in the absence of any chemical reaction, although in such a case the heat effect will in the majority of cases be of quite a different order of magnitude from that which is caused by a chemical reaction.

4. The Freezing Point Equation.

If we combine the purely thermodynamic equation

$$d\pi = \left(\frac{-L_F}{V}\right)\frac{dT_F}{T_F} \tag{82}$$

with our fundamental equation

$$d\pi = \left(\frac{-RT}{V}\right) d\ln N \tag{104}$$

so as to eliminate π, we obtain the desired equation[20]

$$dT_F = \left(\frac{RT_F^2}{L_F}\right)\left(\frac{dN}{N}\right) = \left(\frac{-RT_F^2}{L_F}\right)\left(\frac{dN'}{N}\right). \tag{122}$$

For *very dilute* solutions, we *can* of course substitute the freezing point lowering Δt_F in place of $-dT_F$ and $\frac{n'}{n}$ in place of $\frac{dN'}{N}$ and obtain the familiar law of Raoult-van't Hoff for freezing point lowering in dilute solution:

$$T_0 - T_F = \Delta t_F = \left(\frac{RT_0^2}{L_F}\right)\left(\frac{n'}{n}\right) \tag{124}$$

It is preferable, however, to integrate our differential equation and thus obtain a general equation for an ideal solution of any concentration. Before doing this we will substitute in equation (122)

$$T_0 - \Delta t_F = T_F,\ 1 - N' = N \text{ and } -d(\Delta t_F) = dT_F$$

where Δt_F is the freezing point lowering in centigrade degrees and T_0 is the freezing point of the pure solvent on the absolute scale. This gives us

$$\frac{dN'}{d(\Delta t_F)} = \frac{L_F(1-N')}{R(T_0 - \Delta t_F)^2}. \tag{125}$$

In order to integrate, we must first express L_F as a function of Δt_F which is done by the following purely thermodynamic equation:

$$L_F = L_{F_0} - \Delta Cp_0 \Delta t_F - {}^1/_2\alpha(\Delta t_F)^2 - {}^1/_3\beta(\Delta t_F)^3 - \ldots \tag{85}$$

---

[18] Ikeda, *J. Coll. Sci. Imp. Univ. Tokyo*, 25, Art. 10 (1908).

[19] Dolezalek, *Z. physik. Chem.*, 64, 730 (1908); see also Möller, *Ibid.*, 69, 449 (1909).

[20] This equation was obtained by Boldingh (*Loc. cit.*, p. 61) in the following form:

$$\left(\frac{L_F}{R}\right)\left(\frac{dT_F}{T_F^2}\right) = \left[\frac{1}{(1-N')} + 2aN'\right] dN' \tag{123}$$

where a has the meaning explained in note (14). Boldingh integrated his equation under the assumption that L_F is independent of T.

In this equation L_{F_0} is the molecular heat of fusion of the pure solvent at its freezing point T_0, ΔC_{P_0} is the attendant decrease in the heat capacity of the system and α, β, etc., are constants expressing the dependence of ΔC_P upon the temperature. Combining (85) with (125) we obtain finally (neglecting β):

$$\frac{dN'}{d(\Delta t_F)} = \frac{[L_{F_0} - \Delta C_{P_0} - {}^1/_2\alpha(\Delta t_F)^2](1 - N')}{R(T_0 - \Delta t_F)^2} \qquad (126)$$

This equation can now be integrated. A convenient way to do this is to integrate into a power series in the desired variable by applying McLaurin's theorem directly to the differential equation, carrying the series only so far as the accuracy of the experimental data warrant for the particular case under consideration. For example, in the case of water solutions if Δt_F be known to 0.001°, then for values of Δt_F which do not exceed 7°, the terms containing α, β, etc., are negligible and the application of McLaurin's theorem gives us the equations[21]

$$N' = \frac{L_{F_0}}{RT_0^2}\left[\Delta t_F - {}^1/_2\left(\frac{L_{F_0}}{RT_0^2} + \frac{\Delta C_{P_0}}{L_{F_0}} - \frac{2}{T_0}\right)(\Delta t_F)^2\right] \qquad (127)$$

and

$$\Delta t_F = \frac{RT_0^2}{L_{F_0}}\left[N' + {}^1/_2\left(1 + \frac{RT_0^2\Delta C_{P_0}}{L_{F_0}} - \frac{2RT_0}{L_{F_0}}\right)N'^2\right], \qquad (128)$$

the remaining terms in the expansion not being significant.

If we desire to follow a freezing point curve through a considerable range of temperature, the general integral of equation (126) is more advantageous. The general integral is

$$R \ln (1 - N') = (\Delta C_{P_0} + \alpha T_0) \ln \frac{(T_0 - \Delta t_F)}{T_0} - \frac{[L_{F_0} - (\Delta C_{P_0} + \alpha T_0)\Delta t_F + {}^1/_2\alpha \Delta t_F{}^2]}{(T_0 - \Delta t_F)} + \frac{L_{F_0}}{T_0}. \qquad (129)$$

Equations of this general character have been derived by several observers[22] and the corresponding theoretical curves have been compared with the experimental curves for a number of systems with good agreement. In these comparisons, however, the constants of the theoretical equation have been evaluated from the freezing point data themselves, so that the agreement loses a good deal of its significance.

5. The Boiling Point Equation.

By combining the purely thermodynamic equation

$$d\pi = \left(\frac{L_v}{V}\right)\left(\frac{dT_B}{T_B}\right) \qquad (90)$$

---

[21] The application of equation (127) to the data for aqueous solutions and the interpretation of the results obtained have been discussed by the author in a previous paper (*Technology Quarterly*, 21, 370 (1908)). This application was made on the assumption that the molecular weight of liquid water is 18. Although the results obtained on this assumption were fairly satisfactory up to a concentration of 1 molal, it is clear that a complete study of the behavior of aqueous solutions from the standpoint of the laws of the Ideal Solution must take into account the degree of association of the solvent. Further investigations along this line are now in progress in this laboratory.

[22] *e. g.*, van Laar (*Versl. K. Akad. van Wet.*, Amsterdam, 1903 and 1904; several papers) Roozeboom (*"Die Heterogene Gleichgewicht,"* 2, 267 *et. seq.*), and Yamamota (*J. Coll. Sci. Imp. Univ. Tokyo*, 25, Art. 11 (1908)).

with equation (104) so as to eliminate π we obtain the desired equation

$$dT_B = \left(\frac{RT_B^2}{L_v}\right)\left(\frac{dN'}{N}\right). \tag{130}$$

which for very dilute solutions takes the familiar form

$$T_B - T_{Bo} = \Delta t_B = \left(\frac{RT_{Bo}^2}{L_v}\right)\left(\frac{n'}{n}\right). \tag{131}$$

In order to integrate the differential equation (130) we have only to express L_v as a function of the temperature. The First Law of Thermodynamics gives us the rigorous equation

$$\frac{dL_v}{dT} = c_p - C_P + \frac{L_v}{T} - \left(\frac{L_v}{v}\right)\left(\frac{\partial v}{\partial T}\right)_p \tag{132}$$

by means of which we can calculate the temperature coefficient of L_v. If the vapor behaves as a perfect gas this equation becomes

$$\frac{dL_v}{dT} = \Delta C_P \tag{133}$$

and the methods of integration of equation (130) become perfectly analogous in every respect to those followed in the case of the freezing point equation in the preceding section. It is not necessary therefore to discuss them in detail. The final equations have the same form as the corresponding ones for the freezing point lowering.

6. Chemical Equilibrium.

Two examples will be sufficient to illustrate the method of derivation of the laws which regulate chemical equilibrium in the ideal solution. Let the equilibrium be expressed by the equation:

$$a\mathrm{A} + b\mathrm{B} + \ldots \rightleftarrows m\mathrm{M} + n\mathrm{N} + \ldots \tag{134}$$

(*a*) *The Effect of Concentration.*—The purely thermodynamic equation for the effect of concentration upon chemical equilibrium in a liquid phase at constant temperature and pressure is

$$-aV_{\mathrm{A}}d\pi_{\mathrm{A}} - bV_{\mathrm{B}}d\pi_{\mathrm{B}} - \ldots + mV_{\mathrm{M}}d\pi_{\mathrm{M}} + nV_{\mathrm{N}}d\pi_{\mathrm{N}} + \ldots = 0. \tag{30a}$$

According to equation (104) the osmotic pressure for each substance taking part in the equilibrium is

$$V_{\mathrm{X}}d\pi_{\mathrm{X}} = -RTd\ln N_{\mathrm{X}}. \tag{135}$$

Combining these two equations we obtain the relation

$$\frac{N_{\mathrm{A}}^a \cdot N_{\mathrm{B}}^b \cdots}{N_{\mathrm{N}}^n \cdot N_{\mathrm{M}}^m \cdots} = K_N \tag{136}$$

where K_N is a constant. This expression differs from the Guldberg-Waage Law only in the substitution of the mol fraction N, in place of the volume concentration C. Equation (136) was obtained by Planck[23] as early as 1887, and the reasons for adopting it in place of the Guldberg-Waage form and for expressing the composition of solutions in terms of mol fractions instead of mols per liter were clearly stated by him at the same time.

(*b*) *The Effect of Temperature.*—The purely thermodynamic relation is

$$-aV_{\mathrm{A}}d\pi_{\mathrm{A}} - bV_{\mathrm{B}}d\pi_{\mathrm{B}} - \ldots + mV_{\mathrm{M}}d\pi_{\mathrm{M}} + nV_{\mathrm{N}}d\pi_{\mathrm{N}} + \ldots = \frac{Q_\pi dT}{T}. \tag{38a}$$

---

[23] Planck, *Wied. Ann.*, 32, 489 (1887).

Combining this with equations (136) and (135) and introducing the First Law of Thermodynamics we obtain the equation

$$\frac{d\ln K_N}{dT} = \frac{U}{RT^2} \quad . \qquad (137)$$

which is identical with the van't Hoff Law, with the substitution of K_N in place of the Guldberg-Waage constant K_C. In general it may be stated that the laws for chemical equilibrium in an ideal solution may be obtained from our present dilute solution laws by substituting mol fractions in place of volume concentrations. This applies also to heterogeneous equilibrium. The Solubility Product Law, for example, for a saturated solution of the solute BC which dissociates into B and C becomes[24]

$$N_B \cdot N_C = const. = K_S. \qquad (138)$$

7. Concluding Discussion.

Lest any one from the perusal of the foregoing pages should gain the impression that the problem of a satisfactory general theory of solutions may be regarded as completely solved, it will be well to examine for a moment, in a general way, the characteristics of the Theory of the Ideal Solution with respect to its advantages and disadvantages when regarded as the basis for a general theory of solutions. When compared with the Theory of Dilute Solutions we must acknowledge that it constitutes a distinct and decided step forward. One requirement of a satisfactory general theory of solutions is that it shall represent the facts throughout the whole range of concentrations for some type of solution, at least. This requirement is fulfilled by the Theory of the Ideal Solution and we may feel considerable certainty that any deviation from the requirements of this theory, in a given case, is due to physical or chemical causes and capable of a physical or chemical explanation and is not simply the result of attempting to apply a set of incomplete laws which do not and could not be expected to hold for any kind of a concentrated solution no matter how simple its character.

The success of the Theory of the Ideal Solution as an instrument for throwing light upon the processes occurring in solutions has already been demonstrated in several instances. In the case of several solutions which apparently exhibit a behavior contrary to the requirements of the Theory, Dolezalek[19] has shown that perfect agreement between theory and experiment exist if the assumption be made that a simple compound is formed between the two constituents or that one of them is partially associated. In the case of acetone and chloroform for example, the assumption of a single compound, $CHCl_3(CH_3)_2CO$, and the introduction of the corresponding equilibrium constant into the equations sufficed to produce complete agreement between theory and experiment. It is true that the value of the constant was computed from the vapor pressure data themselves, but in a recent paper[19] Möller has shown that the values of such constants may be obtained independently of the vapor pressure data of the solution under consideration and that they therefore possess the physical significance ascribed to them and are not simply empirical constants of an interpolation formula.

---

[24] This is obtained by combining equations (51) and (104). It does not involve the Mass Action Law [*i. e.*, equation (136)], which is usually assumed as the basis for the derivation of the Solubility Product Law. This point, which was brought out in the previous paper, has been overlooked in all of the textbooks of physical chemistry, although it was explained clearly by Planck as early as 1887 (*Loc. cit.*).

In all the cases studied by Dolezalek he found that agreement between experiment and theory is produced if the assumption be made that what appears to be a deviation from the theory is simply due to the fact that the numbers assumed as the mol fractions of the two constituents in the solution are incorrect and that when the proper mol fractions are used, the apparent discrepancy disappears. If we were justified in assuming that *all* solutions are really ideal solutions and that what appear to be exceptions are merely due to our inadequate knowledge of the number and kind of the various molecular species present and their respective mol fractions, then the Theory of the Ideal Solution would constitute a general theory including all solutions and all concentrations and would enable us to ascertain just what occurs chemically, when the solution is formed out of its constituents. Unfortunately such is not the case, for it can be easily shown mathematically that if certain liquids form an ideal solution with one another they must be miscible in all proportions. The solutions in a system composed of two or more liquid phases in equilibrium with one another cannot therefore be governed to the laws of the Ideal Solution. Moreover, these exceptions are not merely apparent but are real and cannot be explained on the grounds of association, dissociation or chemical combination. The explanation must be looked for in a radical difference in the physical nature of the medium.

To illustrate by an extreme case, let us consider a system composed of a solution of benzene in mercury and a solution of mercury in benzene, both solutions in equilibrium with each other. The vapor pressure of benzene from the mercury layer is equal to its vapor pressure from the benzene layer and yet the mol fraction of benzene in the mercury layer is probably so small that we could not detect it by any analytical means, while in the benzene layer it is equal to 1, within the limits of our ability to measure it. The equality of the vapor pressure from the two layers can only be due, therefore, to the fact that the nature of the medium between the molecules of mercury is such that the benzene molecules can penetrate it only with the greatest difficulty. This effect of the physical nature of the medium is therefore one which must be taken account of in all applications of the Theory of the Ideal Solution. In order that the laws of the Ideal Solution shall apply, the nature of the medium or the field of force in which the molecules find themselves in the solution must not be *very* different from that of the pure liquid itself. Although this restricts somewhat the sphere of usefulness of the theory, there still remain a large number of cases where it should prove of the greatest value in the elucidation of the chemical nature of solutions. Even in cases where the theory cannot be extended over all concentrations because of a consequent radical change in the physical nature of the medium, we may still hope to obtain valuable results with its aid in solutions of moderate concentrations. At all events, I believe that the Theory of the Ideal Solution is the one which should be adopted as the basis for reference, classification and interpretation of the experimental data on solutions in place of our present Theory of the Infinitely Dilute Solution which is only a special, though very important, case of the former theory.

URBANA, ILLINOIS, Feb. 1, 1910.

[FROM THE PHYSIOLOGICAL LABORATORY OF THE CORNELL UNIVERSITY MEDICAL COLLEGE, NEW YORK.]

THE FATE OF THE AMINO ACIDS IN THE ORGANISM.[1]

BY GRAHAM LUSK.

Received February 15, 1910.

Only a few years ago the chemical composition of protein was absolutely unknown. In many quarters the accepted idea was that voiced by Bidder and Schmidt in 1852, namely that all the nitrogen of protein together with enough carbon, hydrogen and oxygen to form urea were split from combination in protein, while the remainder was burned to carbon dioxide and water, thereby yielding heat to the organism. Voit believed that this non-nitrogenous remainder yielded carbohydrate, as was particularly evident in diabetes and also fat. Indeed the conception of the structure of the protein molecule was quite like that which Levene has so splendidly shown to be characteristic of nucleic acid, *i. e.*, a molecule made up of carbohydrate united with phosphoric acid on the one side, and with nitrogen-containing purine and pyramidine bases on the other. The modern conception of the protein molecule as a huge complex of amino acids riveted together dates from the work of Emil Fischer. Fischer has strung together eighteen of these amino acids in an artificial compound, a peptide called *l*-leucyl-triglycyl-*l*-leucyl-triglycyl-*l*-leucyl-octoglycyl-glycine, a body similar to peptone. Already Fischer has prepared over a hundred such artificial polypeptides.

Proteins differ, as they contain different amino acids. Fischer, in an address given in 1907, expressed the opinion that the proteins then known were merely mixtures of substances, and were not pure individuals. He would not attribute all the great multitude of amino acids found on hydrolysis to a single chemical unit. Osborne, however, takes a different view and believes that his beautifully prepared crystals of plant protein "show a constancy of properties and ultimate composition between uccessive fractional precipitations which give no reason for believing the substance to be a mixture of two or more individuals." He adds: "Of twenty-three seed proteins which have been hydrolyzed all have yielded leucine, proline, phenylalanine, aspartic acid, glutamic acid, tyrosine histidine, arginine and ammonia. Glycocoll, lysine and tryptophane are the only amino acids which have been proved lacking in any of these proteins." Other amino acids not mentioned above, but frequently revealed, are alanine, valine, serine, cystine, proline, and oxyproline. The chains of amino acids forming this complex must be of immense size to comprise the many and varied elements set forth above. Osborne calculates the molecular weight of protein at 15000 or some higher multiple of this.

---

[1] A paper read before the New York Section of the Chemical Society, February 11, 1910.

In general, the same constituent amino acids are present in both plant and animal protein. There is no fundamental dividing line. Hence the animal may eat the plant protein, break it by digestion into its constituent amino acids, and then reconstruct these into proteins of another order, those characteristic of animal tissues. Osborne[1] calls attention to the fact that the food proteins which are found in flour are those which are prepared within the endosperm of wheat for the nutrition of the wheat embryo. In the commercial process of milling these embryos are separated and discarded. Bread therefore contains the same nutrient proteins as those provided for the embryo of the wheat.

Osborne finds that seeds which are botanically closely related contain similar food proteins, although those of the leguminous seeds differ greatly from those of the cereals. Hence the developing plant embryo is supplied with a definite food which for each individual of the same species is the same, but for those of different species is different.

It is the same thing in the animal. The genitalia of the fasting salmon grow at the expense of the muscle tissue, as was shown by Miescher, and Jägerroos has adduced evidence which shows that the young of a pregnant dog may be largely nourished at the expense of the protein of the maternal organism. And at all times the unborn animal is furnished with nutrient material of the mother's blood.

Rubner has classified food protein into three divisions representing three varieties of physiological use. The first is the "wear and tear" quota or the amount required to balance the normal waste of tissue protein. The second in the "growth quota," or that necessary for the growth of the body. The third is the "dynamic quota" or that which is used merely to maintain the energy of the cells and whose function may be replaced by carbohydrate or by fat.

In adult life the fundamental use for food protein is to prevent the loss of body protein. If the organism be given fat or carbohydrate alone there will be a constant loss of body protein, the "wear and tear" quota of Rubner. This will continue unless new protein or amino acids are given to replace that lost to the body. Here only the proper array of amino acids will furnish new materials for replacement of the old. For example, if tryptophane be absent from the food, no replacement is possible.

In the growing and even in the adult animal there are conditions in which protein is added to the body. That portion of the food protein retained for growth is the "growth quota." This growth is accomplished at the expense of amino acids formed from ingested protein. Very often protein is taken in excess of that required for the replacement of the "wear and tear" quota and in such excess that the optimum protein content of the cells is reached and no new deposit from the "growth quota" is possible. What then becomes of the excess? Instead of such protein being retained in the organism, it is broken up, its nitrogen is found in the urine as urea, and its deaminized remainder furnishes fuel for the organism. This is the "dynamic quota."

---

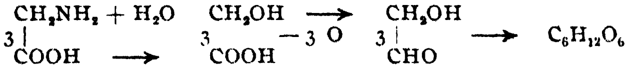
[1] Osborne "The Vegetable Proteins," 1909.

Modern knowledge indicates that the amino-acid nitrogen not used for growth is split off from its combination in the form of ammonia and this ammonia, uniting with carbon dioxide, is carried as ammonium carbonate to the liver and there synthesized to urea. Whenever single amino acids are ingested their nitrogen content appears in the form of urea in the urine. Convincing and recent evidence of this theory is that afforded by Otto Cohnheim, who filled the intestines of fish with albumoses and on suspending the intestines in saline (Ringer's) solution witnessed a large evolution of ammonia. Amino acids similarly treated gave the same results. Very striking also are the experiments of Weinland on the larvae of the blow-fly, which derive their nutriment from meat. These larvae may devour an amount of meat equal to sixty per cent. of their own weight within a space of two days. A large part of this meat protein they convert into fat, the nitrogen content being eliminated as ammonia. When this well-established biological principle of the origin of fat from protein is considered in connection with the fact that in diabetes sugar may arise from protein to the extent of nearly sixty per cent., it becomes evident that there may be a condition of nutrition in which protein is used neither for repair nor for growth, but simply to be deaminized and subsequently to act like fat or carbohydrate as nutritive materials for the organism. This represents the "dynamic quota" of Rubner, the portion of food protein used for energy alone and which may be equally well furnished in the form of fat or carbohydrate.

How, then, does such a conversion of amino acids into carbohydrates and fat occur? To have a complete knowledge concerning this, one must know the fate of each individual amino acid ingested into the organism.

Dr. Ringer and I have recently taken up the subject of sugar production from amino acids. We have given various such acids to diabetic dogs. We have noticed that the nitrogen elimination in the urine increased in amounts which corresponded to that ingested and that this increase was all due to urea nitrogen. We have given glycocoll, alanine, aspartic acid, glutamic acid, containing respectively two, three, four and five carbon atoms. It was found that all the glycocoll and all the alanine were converted into glucose, whereas three of the carbon atoms contained in aspartic and glutamic acids were so converted.

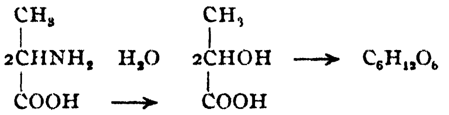
The process of the deamination of these substances is believed to be one of hydrolysis. After this fashion glycolic acid would be produced from glycocoll. If this were converted into glycolic aldehyde, then three molecules of the latter would form one of sugar, and indeed the subcutaneous injection of glycolic aldehyde into a rabbit leads to the elimination of sugar in the urine.[1] These reactions would thus be written:



$$\begin{array}{llll} \mathrm{CH_2NH_2 + H_2O} & \mathrm{CH_2OH} \longrightarrow & \mathrm{CH_2OH} & \\ 3\,| & 3 \qquad -3\,\mathrm{O} & 3\,| & \longrightarrow \mathrm{C_6H_{12}O_6} \\ \mathrm{COOH} \longrightarrow & \mathrm{COOH} & \mathrm{CHO} & \end{array}$$

Glycocoll. Glycolic acid. Glycolaldehyde. Glucose.

Next, in the case of the amino-acid alanine, we found that it also may be completely converted into dextrose. The reaction may involve the production of lactic acid from alanine by hydrolysis and the synthesis of two molecules of lactic acid into dextrose. This reaction would read:



$$\begin{array}{llll} \mathrm{CH_3} & & \mathrm{CH_3} & \\ | & & | & \\ 2\mathrm{CHNH_2} & \mathrm{H_2O} & 2\mathrm{CHOH} & \longrightarrow \mathrm{C_6H_{12}O_6} \\ | & & | & \\ \mathrm{COOH} & \longrightarrow & \mathrm{COOH} & \end{array}$$

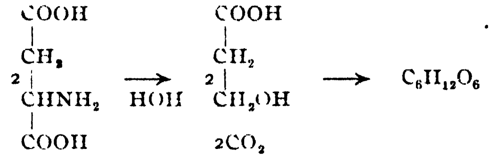
Alanine. Lactic acid. Glucose.

Several years ago Arthur Mandel and I gave a diabetic dog subcutaneous injections of *d*-lactic acid and saw that it was completely converted into glucose. Lactic acid therefore could circulate throughout the body's tissues without being oxidized and when it reached the liver be synthesized to glucose and be eliminated through the kidney of the diabetic. This introduces the question whether lactic acid can ever be directly oxidized by the organism or whether it must not first be converted into glucose. This fate of alanine is also suggested by the work of Neuberg, who gave alanine to a normal rabbit and found glycogen stored in the liver and lactic acid eliminated in the urine. The idea that lactic acid of itself cannot be oxidized accords with the work of Neubauer,[2] which indicates that the deamination of the side chain of tyrosine is not accomplished by simple hydrolysis but by a simultaneous oxidation process, with the production of a ketone instead of an alcohol. The ketone is combustible in the organism, the alcohol not. This reaction will be taken up in connection with the fate of tyrosine. According to this view, pyroracemic acid, $CH_3COCOOH$, would have to be the product of the oxidative deamination of alanine, if the latter were to be directly oxidized. Since the deaminized acid is protected from oxidation, it appears to be probable that lactic acid is the primary product involved in this case. Hence the normal fate of alanine occurs by way of hydrolysis to lactic acid which the organism cannot oxidize except indirectly by synthesis to glucose.

[1] Mayer, *Z. physiologische Chemie, Bd.*, 38, 151 (1903).

[2] Neubauer, "Ueber die Abbau der Aminosäuren," Habilitationsschrift, 1908.

When Dr. Ringer and I gave aspartic acid to a dog with phlorhidzin glucosuria we observed an elimination of extra sugar in the urine equal to the conversion of three out of its four carbon atoms into glucose. The probable course of metabolism in this instance is as follows:

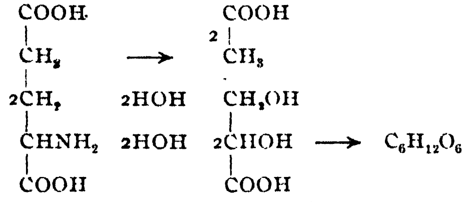


$$2\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CHNH_2}\\ |\\ \mathrm{COOH}\end{array}\xrightarrow{\mathrm{HOH}}2\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2OH}\\ \\ 2\mathrm{CO_2}\end{array}\longrightarrow \mathrm{C_6H_{12}O_6}$$

Aspartic acid β-Lactic acid. Glucose.

It is interesting in this connection to note that Höckendorf[1] has observed an increase in the sugar elimination following administration of propyl alcohol to a phlorhidzinized dog, and although some of his results must be accepted with a certain reserve, Dr. Ringer and I have been able to confirm the above observation. Hockendorf's method of single injections of phlorhidzin each day instead of at eight hour intervals calls for severe criticism.[2]

Concerning the fate of glutamic acid where again three atoms of the molecule go over into glucose, the following argument is proposed. When fatty acids are oxidized in the body Knopp has shown that there is a primary oxidation at the β-carbon atom with a cleavage of acetic acid from the chain, which latter is then readily destroyed. If such a method were employed in the metabolism of glutamic acid, acetic acid and glyceric acid would result, the latter of which might be converted into glucose. The reaction would be as follows:



$$2\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CHNH_2}\\ |\\ \mathrm{COOH}\end{array}\xrightarrow{2\mathrm{HOH}\ \ 2\mathrm{HOH}}\begin{array}{l}\mathrm{COOH}\\ 2\,|\\ \mathrm{CH_3}\\ \\ \mathrm{CH_2OH}\\ |\\ 2\mathrm{CHOH}\\ |\\ \mathrm{COOH}\end{array}\longrightarrow \mathrm{C_6H_{12}O_6}$$

Glutamic acid. Glyceric acid. Glucose.

Ringer and I, in confirmation of this theory, have given a diabetic dog sodium acetate without increasing the quantity of glucose in the urine, whereas the administration of glyceric acid caused a large increase in the output of glucose.

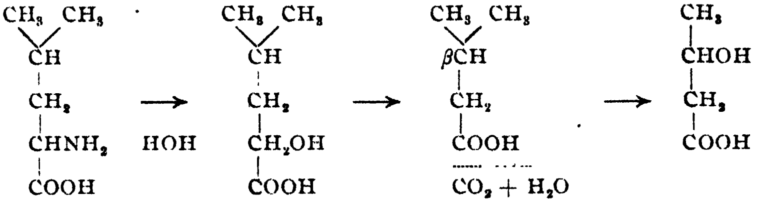
Since serine, on deamination, would be converted into glyceric acid, it is apparent that this amino acid also is probably convertible into glucose.

---

[1] Höckendorf, *Biochemische Zeitschrift* (1909), *Bd.*, 23, 295.

[2] See Stiles and Lusk, *Am. J. Physiol.*, 10, 67 (1903).

Halsey[1] obtained conflicting results after giving leucine to phlorhidzinized dogs, and doubts the conversion of leucine into glucose. Baer and Blum[2] have found an increased output of β-hydroxybutyric acid in the urine after giving leucine to a diabetic man and the following transformation has been attributed to it:

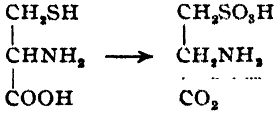


Leucine. Hydroxyisobutyl acetic acid. Isovaleric acid. β-Hydroxybutyric acid.

The fate of *valine* is unknown. Whether it is converted into glucose or not is yet to be determined. Baer and Blum report that it is not convertible into β-hydroxybutyric acid.

Of lysine, a diaminocaproic acid, one can only speculate that it may yield glucose, perhaps to the extent of half of its molecule. Less probable appears the prospect of obtaining glucose from arginine. The metabolism of pyrrole derivatives, such as proline, of indole, of derivatives like tryptophane, or of histidine with its imidazole ring, is too obscurely known to make any prediction.

Cystine, with its sulphur content, is the mother substance of the taurine of the bile and apparently is deaminized less readily than other amino acids. Its conversion into taurine is given by Friedmann as follows:



$$\begin{array}{c} CH_2SH \\ | \\ CHNH_2 \\ | \\ COOH \end{array} \longrightarrow \begin{array}{c} CH_2SO_3H \\ | \\ CH_2NH_2 \\ \text{-----} \\ CO_2 \end{array}$$

Cystine. Taurine.

Any further intermediary products of cystine metabolism are unknown.

Finally there remain tyrosine and phenylalanine to be considered. The fate of these acids has been in part revealed by the work of Neubauer and Falta[3] and of Neubauer[4] alone. Under ordinary circumstances these acids are oxidized in the body with the complete destruction of the benzene ring. The breaking up of the ring in these substances is dependent upon the presence of the amino radicle in the *alpha*-position on the side chain. In a disease called alkaptonuria these substances only reach the homogentisic acid stage and are then eliminated in the urine. Homogentisic acid, which is destroyed by a normal individual, cannot be oxidized by the alkaptonuric patient any more than glucose can be destroyed by the diabetic. The general transformation is as follows:

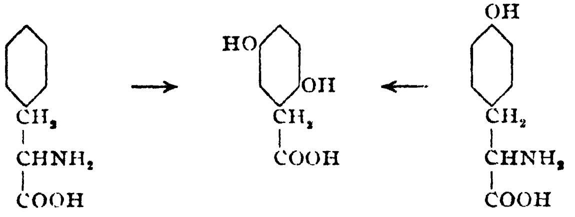
---

[1] Halsey, *Am. J. Physiol.*, 10, 229 (1904).

[2] Baer and Blum, *Arch. exper. Path. Pharm.*, 4, 89 (1906).

[3] Neubauer and Falta, *Z. physiol. Chem.*, 42, 81 (1904).

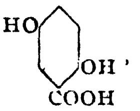
[4] Neubauer, *Loc. cit.*



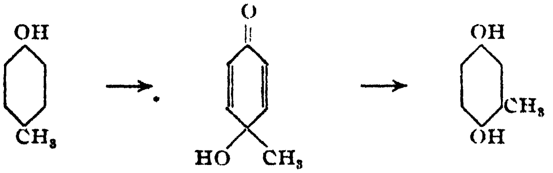
Phenylalanine. Homogentisic acid. Tyrosine.

Neubauer states that the hydroxyl group on the benzene ring must be in the para position, or the transformation into homogentisic acid is impossible.

Neubauer finds that the alkaptonuric has lost the power to break the benzene ring. He confirms this by showing that gentisic acid, is oxidized by the normal individual but is not attacked by a person with alkaptonuria. He is astonished at the discovery that the alcohol, hydroxyphenyllactic acid, which is formed from tyrosine by hydrolytic deamination, is not oxidized into homogentisic acid by the organism, whereas the ketone, oxyphenylpyroracemic acid is so converted. From this he reaches the important conclusion that in this case there is oxidative deamination and not deamination by simple hydrolysis.

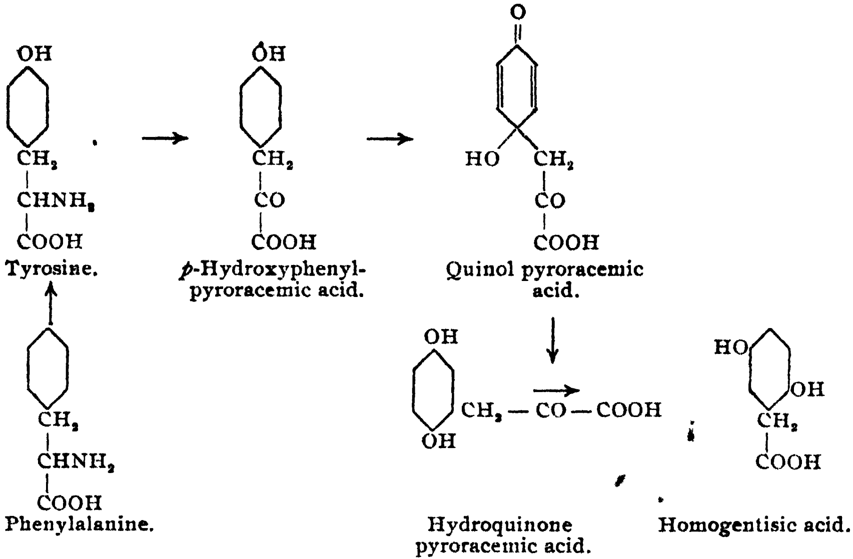


Erich Meyer was the first to call attention to the possibility of the conversion of tyrosine into homogentisic acid through a quinol stage. This is illustrated by the laboratory oxidation of paracresol with per sulphuric acid.



p-Cresol. *p*-Toluquinone. Toluhydroquinone.

The formation of homogentisic acid from tyrosine presents so close an analogy to the above that Neubauer assumes a similar process. The complete reaction would then be:

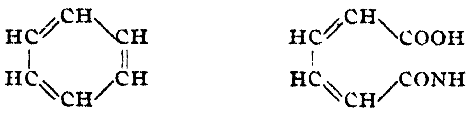


Tyrosine. *p*-Hydroxyphenylpyroracemic acid. Quinol pyroracemic acid.

Phenylalanine. Hydroquinone pyroracemic acid. Homogentisic acid.

It may be of interest to state in passing that this work on the fate of tyrosine was accomplished by a physician in one of the great medical clinics of Germany where opportunities for such work are liberally afforded.

Regarding the further fate of homogentisic acid, the observation of Jaffé[1] that after feeding benzene to animals, muconic acid may be detected in the urine, is of importance. This indicates that the oxidation of the benzene nucleus takes place as follows:



Benzene. Muconic acid.

Should this be the method of breaking the ring, then the straight chain of the dibasic hydroxy acid which would be produced from homogentisic acid would be readily oxidized. It is said that tyrosine, when ingested in diabetes, increases the amount of acetone bodies in the urine (Baer and Blum).

Dr. Ringer and I have investigated the subject of the possibility of its yielding glucose in the body and so far our results have been negative. Since inosite, a hexahydroxybenzene, is completely destroyed by the diabetic, negative results from tyrosine were to have been expected.

In this discussion of the fate of the amino acids in the organism it has been brought out that in their final cleavage products are found either sugar or fatty acid. It is these substances which are the energy givers to the cells. They act as fuel for the machinery of life. In their preparation from protein there are many cleavages, and perhaps oxidations which yield free heat to the organism without ever giving vital energy to the cells. In consequence of this, protein ingestion results in a considerable increase in the amount of heat liberated within the body. This is the *specific dynamic action* of protein in increasing heat production in accordance with the doctrines of Rubner.

---

[1] Jaffé, *Z. physiol. Chem.*, 72, 58 (1909).

As regards the sugar production from meat, for example, one may now in a crude way estimate its source. I have found that in diabetes fifty-eight parts of glucose may arise from one hundred parts of meat protein. Osborne's[1] latest results of the analysis of ox muscle include the following figures:

	Parts in 100
Glycocoll	2.06
Alanine	3.72
Aspartic acid	4.51
Glutamic acid	15.49

In a paper read in Boston recently, Osborne indicated that owing to the inaccuracy of the Fischer ester method, the figures for alanine and aspartic acid may easily be twice the amounts stated above. Likewise, the work of Parker and Lusk indicates that four grams of glycocoll may arise in the metabolism of flesh within the body of a rabbit, and similar results have been obtained in man. If we substitute these increased quantities for the analytical results obtained by Osborne and then calculate the sugar production from the various acids as obtained in the laboratory, we arrive at the following results:

	Parts in 100 of ox muscle (estimated).	Glucose production (calculated)
Glycocoll	4.0	3.2
Alanine	7.5	7.5
Aspartic acid	9.0	6.1
Glutamic acid	15.5	9.5
	36.0	26.3

From these four acids, therefore, may arise twenty-six, or nearly half of the total of fifty-eight parts, of glucose which may originate from protein in metabolism.

Speaking more strictly, forty-five per cent. of the total sugar production from protein in diabetes may arise from the four acids named, which make up thirty-six per cent. of meat protein. It is only a question of time for the attainment of a complete solution of the problem.

The chemistry of the protein molecule throws new light upon biological questions, though it does not explain life itself any more than heredity is explained by the chemistry of nucleic acid.

---

[1] Osborne and Jones, *Am. J. Physiol.*, 24, 437 (1909).

SOME COLLOID-CHEMICAL ASPECTS OF DIGESTION, WITH ULTRAMICROSCOPIC OBSERVATIONS.

By Jerome Alexander

Received February 16, 1910.

The changes which occur during digestion, and in fact in almost all physiological processes, are remarkable not only because of their very profound nature, but also because they are produced at comparatively low temperatures and in the presence of extremely dilute reagents. The living organism disintegrates proteins, oxidizes carbohydrates, and with the same apparent ease synthesizes substances of great complexity. Powerful reagents and high temperatures, which would be destructive to life, are necessary to bring about changes of this character under ordinary laboratory conditions.

The digestive process is preliminary to the actual absorption and use of food by the organism, and has for its object the modification or change of the ingested food into such forms or such substances as may be absorbed in the lower part of the digestive tube. To have a correct understanding of the absorption of the products of digestion, we must bear in mind the fact that the walls of the digestive tract act as semipermeable colloidal membranes, and that absorption consists in diffusion into or through these membranes or their constituent cells. Substances in crystalloidal solution, and colloidal sols whose particles are sufficiently small, represent then the two classes of digestion products which are diffusible and therefore absorbable.

Food as ingested consists mainly of substances that may be grouped into two classes:

1. Crystalloids—such as water, sugars, sodium chloride, etc.
2. Colloids—such as starch, proteins, etc.

The crystalloids are usually absorbed directly, although sucrose, for example, undergoes inversion. The colloids, as a rule, are not directly absorbable and for the most part digestion consists in the disintegration[1] of the colloidal complexes of the food, so that they can actually diffuse into the organism and there undergo further changes. Colloidal gels or even sols whose particles are of large size are, practically speaking, non-diffusible, and must therefore be reduced to a more finely dispersed state. So strong is the analogy between digestion and colloidal disintegration that Thomas Graham,[2] the father of colloid chemistry, coined the word *peptization* to express the liquefaction of a gel. He first speaks of the coagulation or pectization of colloids. "The pectization of liquid silicic acid," he states, "and many other liquid colloids is effected by contact with minute quantities of salts in a way which is not understood. On the other hand, the gelatinous acid may be again liquefied, and have its energy restored by contact with very moderate amounts of alkali. The latter change is gradual, 1 part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry), in 60 minutes at 100°. Gelatinous stannic acid also is easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyzer. The solution of these colloids, in such circumstances, may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid, but alkaline. Liquid silicic acid may be represented as the 'peptone' of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali may be spoken of as the peptization of the jelly. The pure jellies of alumina, peroxide of iron, and titanic acid, prepared by dialysis, are assimilated more closely to albumen, being peptized by minute quantities of hydrochloric acid."

---

[1] It must of course be borne in mind that actual chemical changes may and very frequently do accompany changes of this character.

[2] "On the Properties of Silicic Acid and Other Analogous Colloidal Substances," *Proc. Roy. Soc.*, June 16, 1864.

Investigation has demonstrated that the high efficiency of the digestive juices is mainly due to small quantities of certain colloidal substances called enzymes (such as ptyalin, pepsin, and pancreatin) which act as catalyzers, enormously hastening reactions which would otherwise proceed so slowly that, practically speaking, they would not occur at all. The enzymes appear to act by forming with the substrate a combination of unstable character, which breaks down and liberates the enzyme again to continue the operation.[1] Recently Prof. W. M.

---

[1] In an unpublished thesis presented early in 1899, and read before this section on Dec. 8, 1899, I stated as follows:

"It appears then, that all fermentations are purely chemical changes brought about by substances usually highly complex and highly nitrogenous, as analysis shows. To confirm more fully this assumption, work should be done along the lines laid down by Büchner, and the active enzymes should be isolated from all fermentative micro-organisms. In the meanwhile we may examine into the nature of the chemical action that takes place.

"There are numerous reactions which go by the name of 'continuous processes.' The decomposition of the diazo compounds by cuprous salts (Sandmeyer's reaction) is a case in point. It proceeds according to the equation $C_6H_5N : NR + Cu_2R_2 = C_6H_5R + N_2 + Cu_2R_2$, so that the process is theoretically continuous. The cuprous salt acts the part of a carrier or 'go-between,' just as do iodine, ferric chloride, aluminium chloride and many other substances under different circumstances. The catalytic decompositions of hydrogen dioxide and hypochlorous acid are apparently continuous processes, although the intermediate compounds have not been determined.

"Not alone can only a small quantity of one substance decompose a large quantity of another, but the same substance yields varied products depending on the nature

Bayliss, in his interesting monograph on "The Nature of Enzyme Action,"[1] has shown that in all probability "the 'compound' of enzyme and substrate, generally regarded as preliminary to action, is in the nature of a colloidal adsorption compound." Any one who has seen in the ultramicroscope the extremely active motion of the individual particles in colloidal solutions, can readily imagine the terrific bombardment a substance must undergo when a colloidal enzyme is concentrated on its surface by adsorption; and indeed it seems probable that enzymes actually produce their effects by virtue of their specific surface actions and the motion of their particles.

In order to find out if this idea could be verified by actual observation, I have watched, under the ultramicroscope, the action of diastase upon potato starch grains and the action of pepsin upon coagulated egg albumen.

In the first case actively moving ultramicrons in the diastase solution gradually accumulated about the starch grains, which after a time showed a ragged and gnawed margin. While the adsorption and motion of the larger ultramicrons was all that could be followed, the bright appearance of the field indicated that more numerous finer particles were present, and some apparently of intermediate size were seen.[2]

For observations on albumin, I used a dilute solution of white of egg which had been heated nearly to boiling. It was opalescent and in the ultra apparatus exhibited a field full of bright and rapidly moving ultramicrons. Upon allowing a droplet of essence of pepsin (Fairchilds, containing 15 per cent. of alcohol by weight) to diffuse in, an immediate coagulation occurred, the particles clumping into very large masses. A droplet of decinormal hydrochloric acid was then allowed to diffuse in, whereupon the large masses broke up in small groups and single ultramicrons, which once more resumed their original motion. Soon, however, the albumin particles began to grow smaller and disappear, the field all the while becoming brighter and brighter, indicating the concom-

of the 'go-between.' Ethyl acetoacetate, when hydrolyzed with dilute boiling acids, yields ketones; while if strong alcoholic potash be employed, acids are produced. The latter is not a continuous process because the potash is eliminated by combining with the acid produced; but it illustrates the point.

"Now I believe that the actions of diastase, and in fact of all other enzymes, are in the nature of continuous processes. I base this, as yet, almost entirely upon analogy, but can indicate the line of experimentation necessary to confirm the theory.

"*First*—Active enzymes must be isolated and their chemical constitution and structure investigated.

"*Second*—The constitution of the substances to be decomposed must be understood, and also the nature of the compounds they can form with the structurally determined enzymes."

[1] Longmans, Green & Co., 1908.

[2] This work will be repeated with purer enzyme and at greater dilution.

mitant appearance of smaller ultramicrons or amicrons. *In vitro* the addition of the pepsin to the opalescent albumin solution caused it to clear gradually, even at room temperature [1]

Enzymes are inactivated to a greater or less extent by shaking, heating, electrolytes, etc., all of which, as is well known, cause the coagulation of colloidal solutions and a resulting decrease in the activity of the motion of their constituent particles. Another feature of interest is that the action of enzymes is reversible, a fact that does not usually come much into evidence because of the dilution and removal by diffusion of the products formed. In cells, tissues and organs, however, changes of concentration again occur and synthetic processes may result.

One principle of colloid chemistry is of the utmost importance in digestion, namely, the protective action of reversible colloids, which stabilize or protect from coagulation irreversible or unstable colloids. Mucin and analogous colloidal substances undoubtedly have a function of this character, which may in some cases account for the variance between the action of natural and artificial digestive juices. The principle of colloidal protection[2] is in evidence in almost all physiological reactions and processes, and it is indeed extremely doubtful if there ever occurs *in vivo* any chemical reaction which is not greatly influenced by the colloids always present. How powerful this influence is, may be seen by adding hydrochloric acid to a solution of silver nitrate containing a little gelatin; instead of the usual precipitate, there results only an opalescent hydrosol which passes entirely through filter paper.[3] This directs our attention to a very important consequence of colloidal protection, namely that in the presence of protective colloids, colloidal sols pass through membranes otherwise impermeable to them.[4]

In the light of the principles outlined above, let us consider the digestion of milk, food which contains crystalloids (water, soluble salts, lactose) and colloids (casein, albumin), besides fat in suspension. The main interest centers in the proteins and in the fat, which will be considered in the order given.

The chief proteins of milk are casein and lactalbumin, both of which exist in colloidal solution. In the case of cow's milk the casein is readily coagulated by acids and by the ferment rennin, and therefore such milk curds soon after its ingestion. I will not attempt to mention the numerous and sometimes weird theories advanced to explain the phenomenon

[1] The experiment with pepsin must be repeated with purer enzyme and at greater dilution, in order to follow the course of the action more in detail.

[2] For particulars regarding "protective action," see "Colloids and the Ultramicroscope," by Prof. R. Zsigmondy. J. Wiley & Sons, 1909.

[3] For other reactions of this character, see *J. Soc. Chem. Ind.*, **28**, 280 (1909).

[4] See Zsigmondy, Chapter 14. Mucous membranes, when moistened with bile, allow fat to penetrate more readily than when not so treated (Jacobi).

of the curding of milk, most of which have been considered by Kastle and Roberts in their article on "The Chemistry of Milk."[1] Although many investigators regarded the rennin coagulation of milk as a colloidal or physical, rather than a chemical change, I was, so far as I am aware, the first to point out[2] that casein is an irreversible or unstable colloid which is protected from coagulation by the reversible colloid lactalbumin. A very simple experiment will suffice to show the significance of this fact: if we add to cow's milk some protective colloid such as gelatin or gum arabic, it becomes insensitive to quantities of acid and rennin which would otherwise produce coagulation.

Owing to the very great importance of milk as a food, especially for infants and children, the question of the digestibility of milk has for years received the closest study of the medical profession, and many facts have been established by clinical experiment. Thus, as far back as 1888, Dr. Abraham Jacobi[3] advocated the addition of gelatin and gum arabic to milk intended for infants, and in a recent paper he states:[4] "Ass's milk has always been recognized as a refuge in digestive disorders, when neither mother's or cow's milk or its mixtures were tolerated." These facts are readily understood if we look over the following table[5] showing the average constitution of various milks:

Kind of milk	Casein	Albumin.	Total proteins.	Fat	Sugar.
Cow	3.02	0.53	3.55	3.64	4.88
Human	1.03	1.26	2.29	3.78	6.21
Goat	3.20	1.09	4.29	4.78	4.46
Ewe	4.97	1.55	6.52	6.86	4.91
Mare	1.24	0.75	1.99	1.21	5.67
Ass	0.67	1.55	2.22	1.64	5.99

It will be seen that in mother's milk the casein is protected from coagulation by a much higher ratio of albumin than cow's milk, whereas ass's milk is even more highly protected than mother's milk. With such highly protected milks, the curd (if indeed coagulation does actually occur at all) is much more readily redissolved in the process of digestion.[6]

---

[1] See "Milk and Its Relation to the Public Health," *Bull.* 41, Hyg. Lab. U. S Pub. Health and Mar. Hosp Service, Washington.

[2] *Z. Chem Ind Kolloide*, 4, 86; *C. A.*, 3, 1315; *Z. Chem. Ind. Kolloide*, 5, 101; *C. A.*, 4, 350; *J. Soc. Chem. Ind*, 28, 280 (1909); *C. A*, 3, 1672.

[3] "The Intestinal Diseases of Infants and Children," p. 62, *et seq.*

[4] "The Gospel of Top Milk," *J. Am. Med. Assoc.*, 51, 1216–1219 (Oct. 10, 1908).

[5] Compiled by Leach from Koenig.

[6] Too low a percentage of albumin in mother's milk might make it indigestible for the infant. It is interesting to note here that Dibbelt (*Arb. Geb. path. anat. Bact.*, 6, No. 3, see C. A., 3, 2943) has shown that cases of richitis (rickets) are caused by deficient absorption of calcium, the infants not being able to utilize the larger percentage of calcium in cow's milk and artificial food.

The anomalous results of Kastle and Roberts (*Bull.* 41, 325), who found

Ultramicroscopic observation fully confirms the principle of colloidal protection above stated. Using a Leitz dark field condenser with $^1/_{12}$ oil immersion objective, and a 1200 candle power arc light for illumination, the individual particles of casein may be seen in very active motion. Upon allowing a little dilute acid to diffuse in under th cover glass, the agglutination or coagulation of the casein particles may be distinctly followed. They gather at first into groups of two or three, and gradually into larger and still larger masses. As the size of these groups increases, their motion decreases proportionately, until at last they float quietly and sink to the bottom of the fluid.

If, however, a little gelatin or gum arabic be added to the milk before the addition of the acid, the clumping is entirely prevented. The particles of casein continue the active motion, which in reality keeps them afloat and in solution.

These observations I first made on May 9, 1909, and since then they have been frequently repeated[1] For ultramicroscopic examination a very dilute solution of skim milk (one drop to 100 or 200 cc. of water) should be used, for fat globules, or too great a degree of concentration produce a confused field A very dilute solution of benzopurpurin (which dissolves as a colloid) shows exactly the same protection by reversible colloids as does milk, and in this case the macroscopic color changes as well as ultramicroscopic observation show that gelatin exercises a much greater protective action than gum arabic.[2]

Gelatin also protects casein against coagulation by rennin, as may be shown both in macroscopic and ultramicroscopic observations.[3]

Another very vital point to consider is that the colloidal protection of the casein has an important influence upon the digestion of the milk fat.

In the first place, the initial subdivision of the fat in milk is favored by the "lactalbumen," which acts as an "emulsifier." The use of colloids in forming and preserving emulsions has long been known in the arts and in pharmacy, and has also attracted the attention of physiologists. Thus Moore and Krombholz, in a paper entitled "On the Rela-

---

that frequently quite acid milks did not coagulate, whereas faintly acid milks did, are probably due to the fact that the former owed their stability to a larger relative percentage of albumin than the latter

[1] Exhibited before the Cincinnati Section of the Am. Chem Society on Dec. 8, 1909. Alexander and Bullowa, *Arch Pediatrics*, Jan, 1910. *Ice Cream Trade Journal*, Dec., pp. 197–201, 1909 *Z. Chem Ind Kolloide*, 6, 197–201.

[2] Futher experiments with benzopurpurin, and their significance in dyeing are referred to in a paper submitted to the Seventh International Congress of Applied Chemistry. See *Trans. Am. Inst. Chem. Eng.*, 2 (in press).

[3] See Alexander and Bullowa, *loc. cit.*

tive Power of Various Forms of Proteid in Conserving Emulsions,"[1] state as follows:

"The action of acid and alkali albumins in so maintaining emulsions, must be of service in the digestion and absorption of fats. Protein food is invariably eaten along with fats, and as the fat becomes emulsified, it will be maintained in a finely subdivided form by the action of the acid and alkali albumin simultaneously formed. The fat does not become much subdivided in the stomach, and hence the acid albumin formed here does not come much into action, but afterward in the duodenum the alkali albumin present undoubtedly must aid in preserving the emulsion which is formed there."

The value of an emulsifying colloid is readily demonstrated by adding ferric chloride to a commercial emulsion of cod liver oil; this immediately coagulates the protective colloid and the oil at once separates out. It must also be remarked that protective colloids in the various digestive juices must be reckoned with, as well as those in the food, and those formed from the food.

In the case of milk the presence of a coagulative colloid, casein, introduces another factor, since the curd always carries down with it a very large percentage of the fat present. Now the smaller the degree of colloid protection, the greater is the probability of coagulation, and the less soluble the resulting curd. The total prevention of coagulation is highly desirable, especially in the presence of much milk fat, because fatty curds have a great tendency to adhere and form large masses which resist the action of the digestive juices.[2] In the so-called "fat indigestion" described by Czerny and Keller and others, the trouble has for the most part been ascribed to an excess of fat. But mother's milk, as a rule, contains even more fat than cow's milk, and I have heard of cases showing the typical hard, dry stools of "fat indigestion" where the child was fed cow's milk containing only 2 per cent. of fat. It would seem then that the protection of the casein is of the highest importance in favoring the absorption of the fat as well as the casein of milk.

Interesting confirmation of this is to be found by reading the results of Prof. C. A. Herter, as given in his book on "Infantilism."[1] He describes here a condition of arrested development, consequent upon the non-absorption of food and its subsequent putrefaction in the lower intestine. The patients excreted practically all the calcium ingested, this accounting for the failure of skeletal growth, and the feces contained neutral fat, fatty acids, and soaps in marked excess, indicating impaired fat absorption.[2]

---

[1] *Brit. J. Physiol.*, 22, 54 (1908).

[2] This process is well described by Dr. J. W. Schereschewsky, in his paper on "Infant Feeding," *Bull.* 41, Hyg. Lab. U. S. Pub. Health and Mar. Hosp. Service, p. 658, *et seq.*

In a recent paper entitled "Casein Curds in Infants' Stools," just published in the *Archives of Pediatrics*, 26, 924 (Dec., 1909), Dr. F. B. Talbot states in conclusion: "Furthermore there is sufficient clinical and scientific evidence to prove that tough curds are composed principally of casein, that they are due to the imperfect digestion of casein, and that an excess of casein in the food may result in a fat as well as a casein indigestion."

Herter found that the addition of gelatin (which is a most efficient protective colloid) to the milk fed, caused an improved absorption and recommends its use.[3] He further observes that "in sparing protein small quantities of gelatin appear to have about as much effect as larger amounts," a fact quite in accord with protective action, for only a small percentage of gelatin is needed to accomplish protection.

In conclusion, I would point out that bald chemical analysis cannot express the digestibility and availability of a food any more than it can express or explain the action of the digestive juices, or in fact any other physiological process. In all these processes can be traced the influence of the colloidal substances everywhere present in the body, whose effects are quite out of proportion to their small mass. Striking examples are the enzymes which catalyze and direct chemical and physical changes, and the protective colloids which oppose crystallization, precipitation and coagulation, emulsify fats, and facilitate diffusion and absorption. As soon as we approach the chemistry of living organism, we are confronted with problems of colloid chemistry, and there is no doubt but that a correct understanding and application of its principles will throw much light upon many other obscure problems in biology, physiology and medicine.

LABORATORY OF NATIONAL GUM AND MICA CO., NEW YORK CITY

[FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY OF THE HARVARD MEDICAL SCHOOL.]

ON THE ESTIMATION OF THE INTENSITY OF ACIDITY AND ALKALINITY WITH DINITROHYDROQUINONE.[4]

BY LAWRENCE J. HENDERSON AND ALEXANDER FORBES

Received March 10, 1910

Indicators serve two distinct purposes: The one is to mark sharply an end point in titration, the other to measure the concentration of ionized hydrogen or hydroxyl in solution. The properties which qualify a substance for these two uses are quite different, and usually opposite. Thus our common indicators, selected for use in titration, possess a very limited value in measuring the reaction of a solution, because they change color sharply at a particular reaction, and otherwise not at all. No other means than the employment of indicators permits the rapid estimation of reaction, and even the valuable method of Salm, wherein of necessity a large number of indicators are employed, is far from fulfilling the requirements of a quick method for approximate estimations.

---

[1] "On Infantilism from Chronic Intestinal Infection," by C. A. Herter, M.D. The Macmillan Co., 1908.

[2] It is now well known that the cream layer or fat of milk contains from 10 to 500 times as many bacteria as the whole milk. See (U. S. Dept. Agr.) *Bull.* 56, 737; also Jacobi, *J. Am. Med. Association, loc. cit.*

[3] Herter, *loc. cit.*, pp. 101, 105.

[4] An investigation aided by a grant from the Elizabeth Thompson Science Fund

In seeking a solution of this problem the behavior of 2,5-dinitro-hydroquinone, among other substances, has been studied, its chemical properties being such as to suggest that it might be suitable for the purpose. This substance when dissolved in distilled water, has a bright orange color which changes on addition of moderately strong acid to pale greenish yellow, and on addition of moderately strong alkali to deep purple. Evidently this wide range of colors renders it unusually well suited to the measurement of all intensities of hydrogen ion concentration.

In order more accurately to define the characteristics of the substance and to establish a color standard, the following experiments were performed: A preparation as provided by Schuchardt was twice recrystallized from water to insure purity. From this material a 0.1 molal alcoholic solution was made up and used in all experiments. Six standard solutions of constant reaction were then prepared in the usual manner from simple bases, acids and salts, either pure or mixed, in such proportions that the solutions formed a uniformly graduated scale of acidity on the one side of neutrality, and of alkalinity on the other. The composition of the solutions and their reactions are shown in the accompanying table.

Solution.	Composition.	Reaction.	Color.
A	0.10 *N* Tartaric acid	$(H^+) = 10^{-2}$	Green-yellow
B	0.058 *N* NaH_2PO_4	$(H^+) = 10^{-4}$	Orange-yellow
C	$NaH_2PO_4 : Na_2HPO_4 = 4 : 1$	$(H^+) = 10^{-6}$	Orange
D	$NH_4OH : NH_4Cl = 1 : 27$	$(OH^-) = 10^{-6}$	Brownish cherry-red
E	$NH_4OH : NH_4Cl = 37 : 1$	$(OH^-) = 10^{-4}$	Red-purple
F	1.0 *N* Na_2CO_3	$(OH^-) = 10^{-2}$	Purple

Six 250 cc. flasks were filled from these stock solutions. To each flask was then added a small constant quantity (10 drops) of the indicator solution. The colors of the solutions thus tested are given in the table. Between any two of these colors an intermediate color may readily be distinguished from either, while in those mixtures between orange and purple, where the color change is greatest, several intermediate hues may be differentiated. The indicator has been employed with a variety of salts of the alkalies and the alkaline earths and with ammonium salts, but in no case has an effect of the salt upon the color been noted which is sufficient to cause a significant error in such approximate estimations.

If the indicator be left long in a solution which is even slightly alkaline, as indicated by a reddish color in the solution, or the color of more intense alkalinity, decomposition occurs and the color fades. This destruction occurs too slowly however to cause any trouble. It should be noted that the color varies greatly with the temperature, thus the purple color of high alkalinity may be converted into almost pure blue by warming.

With the aid of this substance it is, accordingly, possible to estimate the concentration of ionized hydrogen and hydroxyl in an unknown solution rapidly and accurately to about one power of ten between hundredth normal concentration of ionized hydrogen and hundredth normal concentration of ionized hydroxyl. In all, eleven different intensities of reaction may be thus differentiated. To this end it is necessary to prepare a series of standard solutions corresponding to those above described The process then consists merely in the matching and interpolation of colors

---

[FROM THE RESEARCH LABORATORY OF THE ROOSEVELT HOSPITAL, NEW YORK CITY.]

THE QUANTITATIVE DISTILLATION OF AMMONIA BY AERATION.

(SECOND PAPER.)

BY PHILIP ADOLPH KOBER

Received February 24, 1910

In a previous paper[1] a new apparatus for the quantitative distillation of ammonia was described, which, since, has been tried in several laboratories. In three cases the results have been published and it is the object of this paper to summarize, and to discuss, the criticisms that have been made, and to record the experience accumulated during the past two years.

In a recent article[2] J. Sebelien in conjunction with A. Brynildsen and O. Haavardsholm developed and reported independently the identical process devised by the writer over a year before.

They proved by many experiments that ammonia can be liberated from solutions quantitatively, even if a slow stream of air and a large volume of solution (200 cc.) are employed. They concluded that the aeration procedure has many advantages over the old method and eliminates several sources of error.

Davis[3] found that the method, using an ordinary water pump, gave good results provided the flask was insulated with asbestos. He also makes the statement that if 30 cc. of acid are digested, the flask would require additional heat during distillation.

---

[1] THIS JOURNAL, 30, 1131 (1908).

[2] Read by J. Sebelien in the Section for Analytical Chemistry, Congress of Applied Chemistry, June, 1909, printed in *Chemiker-Zeitung*, 1909, No. 87.

[3] THIS JOURNAL, 31, 56 (1909).

An asbestos insulator can hardly be of any service in keeping the contents of a flask warm, while a rapid stream of cool air is passing through it. Doubtless, the good results recorded were not dependent on the use of asbestos. That 30 cc. of sulphuric acid can be handled in the process is shown by the figures of J. Sebelien and collaborators. Gill and Grindley have quite recently reported[1] favorably on the process in application to many substances but concluded that the elements magnesium and phosphorus when present together in relatively large amounts cause a slight retention (3.2 per cent.). This conclusion, based on the analysis of cottonseed, wheat bran, and magnesium ammonium phosphate, involves the assumption that magnesium ammonium phosphate, supposedly formed during the digestion, somehow or another, in the strongly alkaline solution holds back the ammonia.

According to modern views of chemistry concerning ions and their concentration it is hard to conceive of magnesium, in a large excess of sodium hydroxide, being in solution at all. In their paper they refer to Steel and Gies[2] having proven it impossible to liberate ammonia quantitatively when the urine contained magnesium and sodium carbonate, but omit to mention that these authors settled the point in question, namely, that sodium hydroxide liberates quantitatively ammonia from magnesium ammonium phosphate. They also refer to a previous paper of mine on the influence of magnesium and calcium salts in retarding ammonia distillation, but surely calcium and magnesium salts cannot come into consideration in an excess of sodium hydroxide.

The figures given by Gill and Grindley record a retention of 3.2 per cent. of the ammonia in magnesium ammonium phosphate, which means that 96.8 per cent. of the ammonia in magnesium ammonium phosphate was distilled and determinable. Taking this value and calculating the amount of ammonia that would be retained from the data given in regard to the content of magnesium and phosphorus in food, etc., we would have in the most unfavorable case a decrease of 0.02 in the per cent. of nitrogen. In order, however, to leave no doubt as to the accuracy of the preceding theoretical discussion the following comparisons[3] were made. A few of them will suffice as they have, apparently, but one interpretation.

	Old distillation with heat, etc.	Aeration after the addition of 5 grams $MgHPO_4$.
Urine No. 1	11.50	11.55
Urine No. 2	11.60	11.60
Urine No. 3	17.35	17.37

The results are expressed in terms of *n*/4 ammonia after making suitable blank determinations, using all the reagents. This amount of magnesium phosphate, being practically ten times more than is sufficient to combine with all the ammonia, does not show the slightest retention.

---

[1] This Journal, 31, 1249.

[2] *J. Biol. Chem.*, 5, 71 (1908).

[3] These distillations were made in the laboratory of Dr. C. A. Herter.

The statement by the authors that it was necessary to keep the solution warm, gives us a key to the source of error, *e. g.*, insufficient excess of alkali.

Experience with the Method.

Since the first publication nearly two years ago the writer has gained considerable experience with the method in the analysis of foods and allied products, particularly in distilling large numbers of solutions in series using but a single ordinary water pump. The time required for complete distillation of ammonia from the long-necked Kjeldahl flask (of 500 cc. capacity) is about two hours, whereas with a large wash bottle (of 700 cc. capacity) the time required is three hours. The time required for aeration varies, as Folin pointed out, with the temperature, alkalinity, volume, and height of the solution.

Saturated alkali in large excess should always be used (about 40 per cent. more than necessary to neutralize the acid). The application of an open-screw pinchcock has made it possible to control the aeration process completely in all respects. Before the addition of the concentrated alkali, this screw pinchcock is applied (at X in the original illustration) at the junction between the Kjeldahl flask and the absorption bottle and the rate of aeration reduced (about 100 bubbles a minute). As the alkali enters the Kjeldahl flask it is shaken in a rotatory fashion until all of the alkali has been drawn over. By decreasing the aeration in this manner it was possible with perfect ease to start a distillation while the contents were still quite hot.

If the aeration is closed off completely at the junction indicated above, the absorption bottle in question can easily be temporarily removed or reinserted, for the purpose of adding more acid, titrating, etc. To avoid accidents a safety valve should be inserted in the system, between the source of vacuum and the first absorption bottle, so that the Kjeldahl flasks are not exposed to too great a vacuum.

Summary of Directions.

The melt in the Kjeldahl flask after digestion is diluted with four parts, by volume, of ammonia-free water and allowed to cool to about room temperature. After connecting to the absorption bottle and reducing the rate of aeration the alkali is added, shaking the Kjeldahl flask at the same time in a rotatory fashion. Should there be any serious back pressure in adding the alkali the rate of aeration is too rapid, and therefore should be reduced to a more suitable rate. The adding cylinder (see first paper) is then disconnected, and the second distillation attached, etc.

THE DETERMINATION OF IODINE IN PROTEIN COMBINATIONS.

(SECOND PAPER.)

BY LOUIS W RIGGS

Received February 24, 1910

During the past three years the study of the iodine content of protein substances, particularly those of the thyroid gland and various thyroid extracts, has been pursued quite steadily in this laboratory with several objects in view. Besides an attempt to determine the relation, if any, of the quantity of iodine to normal and various pathological conditions of the gland, the studies have led to the establishment of certain standards, based on the iodine content, for the grading of thyroid preparations used medicinally. Fundamental to the accomplishment of the objects is an accurate method for the determination of iodine in protein combinations.

During this investigation over three hundred analyses have been made not including duplicates. About one hundred of these were of thyroid glands from as many different human beings. Over eighty were of animal thyroids from dog, beef, pig, and sheep. About sixty were of thyroid extracts such as "thyroglobulin," "thyronucleoproteid," "thyroidine," and medicinal preparations of the gland. A dozen analyses were made of tissues other than thyroid, and about sixty were of mixtures of iodide or iodate with fibrin, heart tissue, pancreas tissue, casein, or other non-iodine containing protein.

The author was led to question the Baumann process by failure to obtain any iodine in nine thyroid glands from patients whose cases were reported as exophthalmic goiter, although iodine was found in glands from twenty similar cases, and also by failure in some instances to obtain concordant results by duplicate analyses of samples from the same gland.

In my previous paper[1] it was shown that more or less of the iodine might be converted to iodate during the fusion process, and consequently not recovered by shaking out with carbon tetrachloride, if the proportion of iodate to iodide be greater than a certain amount, which is perhaps one molecule of iodate to five molecules of iodide. It was also shown that iodate left by the application of Baumann's process could be recovered by reduction.

The present paper furnishes much additional experimental evidence of the necessity for using the reduction process. The objection[2] urged against this process is considered; and analytical data are exhibited from a considerable variety of material.

The essential points of the Baumann process are given in detail in my first paper. In outline they are: fuse the protein with sodium hydroxide and saltpeter to a homogeneous melt, extract the fused mass with water, filter, acidify with sulphuric acid, and shake out with chloroform. The chloroform solution of the free iodine is matched in color by a chloroform extract of a mixture consisting of sodium sulphate, sulphuric acid, sodium nitrite, and a known quantity of iodine as potassium iodide.

---

[1] THIS JOURNAL, 31, 710 (June, 1909).

[2] Seidell, *Ibid.*, 32, 1326 (Dec., 1909).

The most important modifications of the Baumann process suggested in my first paper are: Use of carbon tetrachloride in place of chloroform. Use of 10 cc. Nessler tubes of *white* glass in which 10 cc. of liquid makes a layer 10 cm. deep. Use of a fusion extract of a non-iodine containing protein instead of plain sodium sulphate for the preparation of standards. After the completion of the analysis by Baumann's method, the acid aqueous liquid, from which free iodine had been removed, was made alkaline, reduced with Devarda's alloy, filtered, acidified with sulphuric acid, sodium nitrite added, any free iodine shaken out with carbon tetrachloride and read against standards made from the reduction products of Devarda's alloy and a known quantity of iodine.

Several investigators have reported the finding of thyroid glands free from iodine, and theories have been constructed with reference to the function of "iodine-free thyroid." In the analysis of over one hundred and eighty thyroid glands in this laboratory I have yet to find one free from iodine. If, however, I had used the Baumann process *without* the reduction feature, I could have reported more than a dozen glands as iodine-free. Table I exhibits some of these results

In Tables I, II, III, IV, and VI the figures have been calculated from the readings to milligrams of iodine per gram of fresh gland or fresh proteid. In Table V, the figures mean total quantity of iodine in milligrams in the sample used for analysis. The term "trace" wherever used in this paper means less than 0.01 mg. of iodine in 10 cc. of carbon tetrachloride. The untrained eye can readily appreciate 0.01 mg. of iodine in 10 cc. of carbon tetrachloride when looking through a column of the liquid 10 cm. deep at a white ground. Where percentages are given, traces are discarded in the calculations.

TABLE I

No	Before reduction.	After reduction	No	Before reduction.	After reduction.
1	trace	0.032	7	0.0	0 035
2	0 0	0 011	8	0.0	0.0025
3	0 0	0 013	9	0.0	0 01
4	trace	0.022	10	trace	0 034
5	trace	0 03	11	0.0	0 043
6	0 0	0.01	12	trace	0 026

Nos. 1 to 9 represent pathological human thyroids analyzed in 1907, using zinc dust as a reducing agent. It is possible that if Devarda's alloy had been used larger quantities of iodine would have been recovered. Some of these glands weighed from 150 to 200 grams so that although the weight of iodine per gram of fresh gland was small, the total quantity was in some cases equal to that frequently found in normal glands. Nos. 10 to 12 represent sheep thyroids very poor in iodine.

Seidell suggests that the iodine which I found by reduction was that left in the aqueous liquid by imperfect extraction, although in the thirty analyses reported in my previous paper I used two portions of carbon tetrachloride of 10 cc. each, while he claims complete extraction with three portions of two or three cc. each. A few careful analyses in which more iodine was found after reduction than before would be sufficient to show the error of the foregoing suggestion. In twenty-five analyses I find more than 50 per cent. of the iodine by reduction.

Again if the iodine obtained by reduction be due to imperfect removal of the free iodine by the *first* extraction with carbon tetrachloride, then the greater the quantity found before reduction, the larger the quantity left by imperfect extraction to be recovered by reduction. Table II exhibits the analytical results upon glands rich in iodine in which none or but traces were found by reduction.

TABLE II.

No	Before reduction.	After reduction	No.	Before reduction	After reduction
1	0.47	trace	7	0.36	0.0
2	0.30	0.0	8	1.67	trace
3	0.34	0.0	9	0.97	trace
4	0.70	trace	10	0.30	0.0
5	0.65	0.0	11	0.71	trace
6	1.33	trace	12	1.04	0.0

In these cases where the largest absolute quantity of iodine should be found by reduction, if Seidell's assumption be well founded, I find none or but traces.

In my previous paper it was stated that the most accurate readings were obtained when 10 cc. of carbon tetrachloride contained from 0.02 to 0.15 mg. of iodine. (It is my practice to select such an aliquot part of the fusion extract as will bring the readings within these limits mentioned.) But four of the readings of the thirty analyses of thyroids reported in that paper were above 0.15. Two were 0.16, one 0.20, and one 0.21. The average reading for the thirty was 0.11 mg. In each of these thirty analyses the acid aqueous liquid, which generally measured about 20 cc., was extracted with a second 10 cc.[1] of carbon tetrachloride to remove possible traces of iodine left by the first extraction before applying to reduction process. This detail was overlooked by Seidell in his reference to the reduction process.

In order to determine the quantity of iodine left in 20 cc. of the acid aqueous liquid after *one* extraction with 10 cc. of carbon tetrachloride the following experiment was performed: Ten cc of an iodine-free fusion extract were placed in each of six separators marked respectively *A*, *B*, *C*, *D*, *E*, and *F*. To each separator were added 0.2 mg. of iodine as potassium iodide, 1 cc. of a 1 per cent solution of sodium nitrite, 10 cc. of carbon tetrachloride, and about 7 cc. of 10 per cent. sulphuric acid which was enough to cause a strong acid reaction. The separators were then vigorously shaken with care to prevent loss by the escape of carbon dioxide. After three shakings at intervals of ten to fifteen minutes the carbon tetrachloride was drawn off from each separator as completely as possible. Ten cc. of fresh carbon tetrachloride were then added to the contents of separator *A*, thoroughly shaken, filtered into a 10 cc. Nessler tube, compared with standards and found to contain much less than 0.01 mg. of iodine. This portion of carbon tetrachloride, which had made the *second* extraction of the acid aqueous liquid in *A*, was then added to the contents of separator *B*, shaken out and added to *C* and so on until the acid aqueous liquid in each of the six separators had been subjected to its *second* extraction by the same 10 cc of carbon tetrachloride. From the last separator (*F*) the carbon tetrachloride was filtered into a Nessler tube, compared with standards, and found to contain 0.03 mg. of iodine, from which I conclude that approximately 0.005 mg. of iodine is left in 20 cc. of acid aqueous liquid, originally containing 0.2 mg. of iodine, after iodine is removed by the *first* ten cc of carbon tetrachloride. This result was obtained before the publication of my previous paper. It has since been confirmed by two repetitions with concordant results.

---

[1] THIS JOURNAL, 31, 712, line 7 and line 39.

The acid aqueous liquid in the six separators was then subjected to a *third* extraction with 10 cc. of carbon tetrachloride, performed in the same manner as the second extraction already described, and found to contain *no iodine.*

If 20 cc. of acid aqueous liquid contain *less* than 0.2 mm. of free iodine, less will be left after the first extraction thus making a second extraction quite superfluous. Experiment confirms this statement. Several samples of acid aqueous liquid containing from 0.1 to 0.15 mg. of iodine, when extracted with a second 10 cc. of carbon tetrachloride, gave a liquid that could not be distinguished from 10 cc. of the pure reagent by several observers each accustomed to colorimetric reading.

The results of the application of this process to other glands, in which the presence of iodine might be suspected, are shown in Table III.

TABLE III.

No.	Before reduction	After reduction	No.	Before reduction.	After reduction.
1.	0.0	0.0	4	0.0	0.0
2.	0.0	0.0	5	0.0	0.0
3.	0.0	0.0	6	0.0	trace

No. 1 was a thymus gland from a child one year old, 2 and 3, thymus glands from adults, 4 and 5, beef parathyroids, and 6 a human hypophysis. The record exhibited in Table III at least serves as a check on the purity of the reagents used in this investigation.

The analyses shown in Tables IV and V were made by Miss Van Alstyne of this laboratory and to whom I wish to express my thanks. The determinations of iodine recorded in Table IV were incidental to physiological studies on the storing of iodine in the thyroid gland by dogs; and those of Table V to the standardizing of thyroid preparations used medicinally.

TABLE IV

No.	Before reduction	After reduction	No.	Before reduction.	After reduction.
1	3.59	0.0	6	trace	0.50
2	0.87	0.0	7	0.05	0.03
3	0.46	0.0	8	0.06	0.19
4	9.32	0.0	9	0.52	0.17
5	4.37	0.0	10	0.25	0.16

Twenty-four other determinations of iodine were made in the course of this investigation, fourteen of which gave other 5 per cent. of the iodine by reduction, while four gave all of the iodine *before* reduction. The extremely large quantities of iodine in Nos. 1, 4, and 5 were produced by previous iodine feeding.

TABLE V

No.	Before reduction.	After reduction.	No.	Before reduction	After reduction.
1	0.58	0.30	4	2.10	0.36
2	trace	0.18	5	0.38	0.025
3	trace	0.02			

Table VI shows the results of the analysis of various fractions of human thyroproteins by Dr. Beebe whom I again wish to thank for many favors.

TABLE VI.

No.	Before reduction.	After reduction.	No.	Before reduction.	After reduction.
1	0.68	0.19	4	0.30	0.43
2	0.80	0.20	5	0.27	0.18
3	0.22	0.39			

The figures exhibited in Tables IV, V, and VI clearly demonstrate that when 10 cc. of carbon tetrachloride are used with about 20 cc. of the acid aqueous liquid, imperfect extraction of iodine as suggested by Seidell in no way accounts for the results.

A partial summary of the author's work on the determination of iodine in the thyroid presents the following points: 14 out of 40 glands containing *more* than 0.25 mg. of iodine per gram of fresh gland gave above 5 per cent. of their iodine by reduction. Average of the 14 was 14.2 per cent. 38 out of 59 glands which contained *less* than 0.25 mg. of iodine per gram of fresh gland gave above 10 per cent. of their iodine by reduction. Average of the 38 was 55.2 per cent. Excluding from the 38, 13 glands which gave all of their iodine by reduction and the average percentage of iodine obtained by reduction from the remaining 25 glands was 31.9 per cent While this summary emphasizes the necessity of applying the reduction process to glands poor in iodine, particular analyses show that glands rich in iodine may sometimes yield a considerable quantity of their iodine by reduction.

The experimental results of this paper thoroughly confirm the statement of my previous paper, namely: that more or less iodate is usually present and that in an accurate determination of iodine in protein combinations it is never safe to omit the reduction feature. These results are not explained by the statement "at extreme dilution the constancy of distribution coefficients disappears," which Seidell invokes.

In attempting to follow Seidell's interpretation of Baumann's process, I find it impossible to be certain of several details. Seidell refers to Baumann's earlier process,[1] instead of his later improved process.[2] A very important and essential part of the process as described in both of Baumann's papers is made optional, thus, Seidell directs, "If much charred organic matter is present a little sodium nitrate may be added," etc., from which one would infer that the addition of a nitrate during the fusion is not required, and in the absence of "much charred organic matter" unnecessary. I find a loss of about one half the total iodine to follow the omission of nitrate during the fusion process in two analyses of sheep thyroid rich in iodine.

Baumann, Oswald, Anten, Marine and Wells, working with similar quantities of protein material to those used by Seidell, employed 10 cc. of solvent (chloroform or carbon disulphide) to extract the iodine from the acid aqueous liquid. If this liquid be extracted with only two or three cc. of solvent instead of 10 cc , it would be expected that a considerable portion of iodine would remain to be extracted by further applications of fresh solvent. Although it is well known that two portions, say 5 cc., of solvent successively applied will dissolve slightly more solute than one portion of 10 cc., it is not clear wherein three successive applications of 2 or 3 cc. of solvent confers accuracy upon this process, especially in view of the fact that one application of 10 cc. of solvent removes 97.5 per cent. of the iodine from the maximum concentrations used by the present writer.

The statements by Seidell that "the reduction process as suggested by Riggs leads to greater errors in the determination of iodine than are inherent in the Baumann process" and "any iodine not removed before the reduction process leads to a positive error" are totally unsupported by experimental evidence.

---

[1] *Z. physiol. Chem.*, 21, 489.

[2] *Ibid.*, 22, 1.

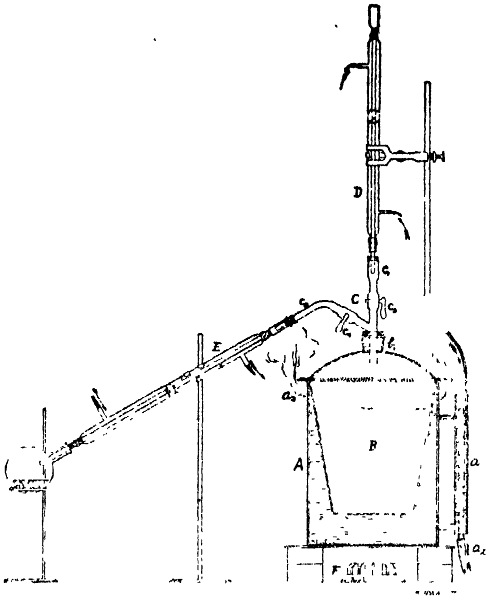
DEPARTMENTS OF CHEMISTRY AND EXPERIMENTAL THERAPEUTICS,
CORNELL UNIVERSITY MEDICAL SCHOOL,
NEW YORK CITY.

AN APPARATUS FOR ABSOLUTE ALCOHOL.

BY W. H. WARREN.

Received March 12, 1910.

Freshly prepared absolute alcohol is more reliable than the article supplied by dealers and much cheaper. One never feels quite sure without making a test that he is getting an alcohol which is really absolute. For preparing small quantities of this solvent there is no need of suggesting any modification of the usual procedure of boiling ordinary alcohol over burnt lime in a glass flask under a return-condenser and distilling. But large classes of students often require considerable absolute alcohol, the preparation of which has to be left to persons more or less inexperienced. Under these conditions there is frequent breakage of glass together with loss of alcohol, and another form of apparatus is desirable. For some time the apparatus shown in the drawing has given satisfactory results in this laboratory. It is constructed of copper and was made according to specification by the firm of Eimer and Amend, New York. A tinsmith can make a less expensive apparatus of heavy tin which will answer every purpose.



The outer flanged copper vessel *A* has an inside diameter of 28 cm. and is 30 cm. high. It is tinned on the inside and the bottom is reinforced on the outside with iron for protection against heat. This vessel serves as a water-bath in which water is kept at constant level by means of the side tubulus a_1 provided with the overflow pipe a_2. The water which passes through condenser *D* runs into a_1. Several openings a_3 at the top allow steam to escape. This bath rests upon bricks and heat is applied from the Fletcher burner *F*.

Within *A* and resting quite free upon its flange is a second flanged copper vessel, *B*. Except for the opening b_1 for introducing burnt lime and alcohol, this inner vessel is closed. It is 24 cm. in diameter and 28 cm. high to the flange. The diameter of the opening b_1 is 57 mm. When filled with burnt lime, *B* holds about nine liters of commercial grain alcohol.

A brass Y-tube *C* passes through a rubber stopper in b_1. The arm c_1 is straight and somewhat widened at the top to admit the rubber stopper connecting it with condenser *D*, but the arm c_2 is bent at an obtuse angle. On each arm beyond the point of divergence is a cock c_3 and c_4. The internal diameter of these tubes is 15 mm., but a somewhat larger bore would be an advantage. Of especial importance is the bore of the cock which should be the same as that of the tube. If the bore of the brass tube is too small, or the cock has a smaller bore than that of the tube, alcohol will collect in the condenser during dehydration.

Condenser *D* is connected with the top of c_1 by a rubber stopper. It should be long enough to cool well during dehydration and its bore should not be too small. Condenser *E*, connected with c_2 by a rubber stopper, is in the usual position for distilling

By closing cock c_4 and opening cock c_3, alcohol can be boiled until dehydrated. It is well to watch the apparatus closely until boiling proceeds quietly. If heated too rapidly, or if the still is too full, alcohol is apt to start boiling so violently that it will be ejected from the top of the condenser. But this occurrence can be avoided by raising the temperature gradually. When boiling begins, the flame can be adjusted and further attention is unnecessary.

By closing cock c_3 and opening cock c_4, a test portion of alcohol may be distilled at any time and its specific gravity determined. If dehydration is incomplete, the test portion may be returned through the top of the condenser. By reversing the cocks, boiling may be continued until a sample having a satisfactory specific gravity is obtained. Finally, when dehydration is complete, distillation may be begun without first cooling the alcohol. Of course all precautions should be taken to keep the distillate from absorbing moisture from the air.

A change in the construction of the still, which would probably be an improvement, may be suggested. When distillation begins and for some time after, alcohol comes over readily, but toward the end it distils slowly. Undoubtedly this is due to the size of the still, which, though well heated on the side and bottom, is not so on the inside. If four or five tubes, closed at the upper and open at the lower end, were to project from the bottom into the interior of the still, the boiling water in these tubes would convey heat into the mass of alcohol and lime and hasten distillation.

Several experiments were made with this apparatus to determine how long to boil alcohol over lime before distilling. I have heard instructors advise half an hour's boiling as sufficient, whereas others have insisted that boiling over lime should be continued for a day at least. The tests I have made with this apparatus would seem to indicate that the longer rather than the shorter boiling is advisable. In making these tests there was no intention of entering upon an investigation of absolute alcohol, but merely of determining the proper conditions for preparing absolute alcohol for laboratory purposes so that definite directions might be given to an assistant having charge of such work.

A pycnometer holding 50 cc. was used in determining all specific gravities. The weight of pure water at 15° C. was first determined in this apparatus and then the weight of an equal volume of alcohol at the same temperature. Specific gravities were compared with those given by Squibb and percentages were calculated from his tables.

Experiment 1.—Small pieces of burnt lime were put into the still to within an inch of the flange, and covered with nine liters of commercial grain alcohol. This alcohol is said to contain 188 per cent. of proof spirit. Its specific gravity was found to be 0.8198 (= 91.04 per cent. by weight). Before being heated, the alcohol stood in contact with lime for twenty-four hours. At the end of that time heat was applied and from the moment the alcohol began to boil, a test portion (about 250 cc.) was distilled every fifteen minutes and its specific gravity determined. The results of these tests are given in the following table:

No	Time of boiling in hours.	Sp. gr at 15° by pycnometer.	Per cent of alcohol by weight
1	0.25	0.7988	98.41
2	0.5	0.7972	98.91
3	0.75	0.7965	99.13
4	1.0	0.7958	99.35
5	1.25	0.7952	99.55
6	1.5	0.7950	99.61
7	1.75	0.7949	99.65
8	2.0	0.7945	99.77

Most of the alcohol after the eighth sample, which contained 99.77 per cent., was distilled into a large bottle. Its specific gravity was 0.7943 (= 99.84 per cent.). The final 500 cc. of alcohol was collected by itself and had a specific gravity of 0.7940 (= 99.94 per cent.). Nine liters of 91.04 per cent. commercial grain alcohol usually yield about six liters of absolute alcohol which will vary slightly in strength depending upon the length of time the alcohol is boiled over lime. From these tests the conclusion was drawn—and this conclusion was confirmed by later tests—that two hours' boiling is by no means sufficient to get the best possible absolute alcohol.

Experiment 2.—Nine liters of commercial alcohol were placed in the still with lime, and boiled for two hours without being allowed to stand as in the first experiment. At the end of that time a sample of alcohol was distilled and tested. This was repeated at the end of each succeeding hour and the results are given in the following table:

No	Time of boiling in hours	Sp gr at 15° by pycnometer	Per cent of alcohol by weight
1	2	0.7964	99.16
2	3	0.7954	99.48
3	4	0.7944	99.81
4	5	0.7943	99.84
5	6	0.7942	99.87
6	7	0.7942	99.87
7	8	0.7942	99.87

The experiment had to be stopped at the end of the eighth hour The remainder of the alcohol stood in contact with lime about 30 hours when boiling was resumed. At the end of an hour's boiling a sample was taken and found to have sp. gr. 0.7942 (= 99.87 per cent.). From this experiment it would appear that when the alcohol reaches the point where it gives a distillate containing 99.87 per cent., it remains constant. This point in this experiment was reached after six hours' boiling. Yet the mass of the alcohol shows a higher percentage, for most of the alcohol as in the first experiment was collected in a large bottle and had a specific gravity of 0.7940 (= 99.94 per cent.). The final portion of distillate was collected by itself but its specific gravity was the same as that of the main sample.

Experiment 3.—The two preceding experiments show that alcohol after twenty-four hours standing over lime will give a distillate at the end of two hours' boiling, containing 99.77 per cent.; whereas the same alcohol that has not stood will give, after being boiled two hours, a distillate containing 99.16 per cent. This seemed to indicate that previous standing over lime might be of advantage. This experiment was made to see if this is the case.

Nine liters of alcohol stood over lime twenty-four hours. At the end of that time the alcohol was boiled two hours and then tested A test was also made at the end of each succeeding hour with the results given in the following table:

No	Time of boiling in hours	Sp gr. at 15° by pycnometer	Per cent. of alcohol by weight
1	2	0.7952	99.55
2	3	0.7950	99.61
3	4	0.7943	99.84
4	5	0.7942	99.87
5	6	0.7942	99.87

From this experiment it would appear that alcohol, which has previously stood over lime, can be brought to the point where it will give a distillate having a constant specific gravity sooner than it can if not allowed to stand; but the difference in time is so slight that there is no advantage in the previous standing.

Experiment 4.—The quantity of burnt lime in the preceding experiments is much in excess of that theoretically needed to take up the water present. Consequently, the yield of absolute alcohol is not as high as it would be if less lime were used. In the hope of increasing the yield without lowering the strength of the alcohol, I made two tests conducting dehydration in two stages and each test gave essentially the same result.

Nine liters of commercial alcohol were boiled for six hours over 2100 grams of burnt lime. This is slightly more lime than is required to take up the water. The specific gravity of a sample of alcohol at the end of six hours' boiling was 0.8006 (= 97.83 per cent.) and that of the entire distillate was 0.7980 (= 98.66 per cent.). The total distillate measured 7450 cc.

I then returned the 7450 cc. of partially dehydrated alcohol to the still with 300 grams of burnt lime, a quantity slightly in excess of that theoretically needed to combine with the water. The specific gravity of the total distillate after six hours' boiling was 0.7970 (= 98.97 per cent.) and it measured about 7300 cc.

The yield of absolute alcohol by this method is much better but twice as much time is required and the alcohol, though sufficiently good for most purposes, is by no means as nearly absolute as it is after one treatment with a large excess of lime.

Summary.

1. It is not possible to deprive commercial alcohol of all its water by boiling over lime. Dehydration takes place gradually up to a certain point and it is useless to boil longer under return-condenser when the test-distillate contains 99.87 per cent.

2. Commercial alcohol can be brought to the point where it will give a test-distillate containing 99.87 per cent. by boiling six hours without previous standing over lime; or, by boiling five hours, after allowing the alcohol to stand for twenty-four hours over lime.

3. When the test-distillate contains 99.87 per cent., the alcohol, if distilled, will contain as a whole 99.94 per cent. I have never succeeded in getting a distillate containing a higher percentage of alcohol than this.

4. It is possible to increase the yield of absolute alcohol by conducting the dehydration in two stages and using each time a quantity of lime only in slight excess of that theoretically required to combine with the water present. But the absolute alcohol obtained will by no means be as strong as it will be if dehydration takes place at one operation in presence of a large excess of lime.

WASHINGTON UNIVERSITY MEDICAL SCHOOL,
ST. LOUIS, MO.

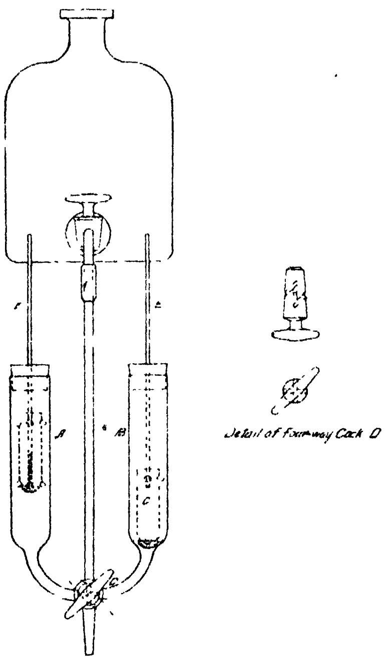
NOTE.

An Adjustable Automatic Burette.—While working at the Minnesota Experiment Station in 1906 on a large number of nitrogen determinations, it was found that the method of measuring the acid and alkali was slow, inaccurate, and not at all neat. The need of something of an automatic nature was felt, but nothing could be found in any of the catalogues of apparatus.

Work was started on a device which would be automatic and also adjustable. The first ones which were made according to drawings failed in the second requirement. However, the idea was not abandoned, and early this year a new form of float was conceived. This solved the difficulty effectually.

Two of the burettes have been at work in this laboratory for some time. One measures 20 cc. of concentrated sulphuric acid and the other 50 cc. of concentrated sodium hydroxide. They have made some 700 measurements very successfully. The percentage of error is so small as to be disregarded.

Since devising the above apparatus, there have come to my notice descriptions of two automatic pipettes. One devised by H. S. Bailey was described and illustrated in THIS JOURNAL.[1] However, it is not adjustable and allows of greater error in measurement. The other is by Professor G. E. Patrick and fully described in Bulletin 19, Iowa Agricultural Experiment Station, November, 1892. This one is adjustable, but to only a limited extent.



Adjustable Automatic Burette Pat Appld for
J O Rose inventor

Believing that the burette herein described does not possess the faults above mentioned, I herewith submit it with the hope that it may find general use in laboratories, creameries, and, perhaps, in some manufacturing establishments.

By referring to the figure, it is seen that the construction is very simple.

---

[1] 30, 1508 (1908).

Two tubes are connected at their lower extremities by a four-way stopcock, *D*, to the supply tube above and the delivery tube below. This stopcock is bored in such a way that the exit of a hole is 90° from the entrance. 90° further around is the entrance of the other hole, which, in turn, is the same distance from its exit. In this way each passage can be made to communicate with either side, *A* or *B*, of the burette by merely turning the stopcock one-quarter turn to the right or left. The position of the hole, or passages permits of the filling of one side and the emptying of the other simultaneously, so that while one charge is being delivered another is being measured.

Control of the liquid is secured by means of open floats, *C*, containing a small quantity of mercury, which act as a seal on the bottom of the glass tube, *E*. These tubes, *E*, allow the passage of air to and from the burette They are adjustable up and down and permit of the calibration of the burette to such quantities as may be desired within the limits of the burette.

The liquid is taken out of the supply bottle by means of a siphon or a tubulature at the bottom. In either case a stopcock is interposed between the supply and the burette merely as a means of safety.

The apparatus is by no means flimsy and can be made for a reasonable price, within the reach of any laboratory. It is the intention, also, to adapt the apparatus for industrial work where it is required to mix definite volumes of liquids repeatedly. J. D. Rose.

Cereal Laboratory, University of California

REVIEW.

RECENT WORK IN BIOLOGICAL CHEMISTRY.

By Carl L. Alsberg.

Received March 5, 1910

Four years ago, in This Journal, P. A. Levene began his résumé of biochemical literature with the statement that work in biochemistry had enormously increased. This is true to a very much greater degree to-day, as is evidenced by the establishment since Levene wrote of three new journals: *viz.*, *Zeitschrift fur Biochemie*, *The Biochemical Journal*, and the *Journal of Biological Chemistry*, though one of the old journals (*Hofmeister's Beiträge*) has been merged with the first of the three. It will therefore be utterly impossible in the space at my disposal to consider more than a fraction of the important publications which have appeared since Levene's review. One of the notable factors in this enormous increase in biochemical work is the tendency of organic chemists again to take for the subject matter of their research substances occurring in living things, as was the custom more than a generation ago before the great expansion of synthetic organic chemistry. Therefore the last years are characterized by the determination of the constitution and sometimes by the synthesis of bodies already known rather than the discovery of new bodies. This is particularly true of protein chemistry. No new ultimate component of protein has been discovered despite the calculation of Osborne, Leavenworth and Brautlecht that about 14 per cent. of the nitrogen is still unaccounted for.[1] Abderhalden, Levene, and Osborne with their collaborators, as well as others, have continued to make us acquainted with the amino acids of a large number of proteins; but their hydrolyses have not led to the discovery of any new amino acids. The important fact has come to light that some amino acids are absent in some vegetable proteins. Rye, wheat, and barley gliadin and zein lack lysine and are poor in arginine and histidine, while zein also lacks glycocoll and tryptophane.[2]

The old problem as to whether homologous proteins from different species are chemically identical, has again been attacked, chiefly by Osborne and to a less degree by Abderhalden. The method consisted in determining as quantitatively as possible the amino acids obtained on hydrolysis and comparing the results. Osborne and Clapp[3] compared the gliadin from wheat, rye, and barley, and found them very similar, corresponding to the close genetic relationship of these plants. On the other hand Osborne and Heyl[4] found that the legumin from the veitch and pea are probably not identical. Abderhalden and Schittenhelm chose the caseins from different milks and found that in cow's, goat's and probably also in woman's milk the component amino acids are so similar quantitatively and qualitatively that one is not justified from these data alone in concluding that there is any difference.[5] Now it is very probable from more purely biological considerations that some proteins which yield the same amino acids on hydrolysis, must nevertheless be different. It appears that sometimes it is not enough to know the component amino acids. It is necessary to know also the ways in which they are linked together. Fischer and Abderhalden,[6] Abderhalden[7] and also Skraup[8] have approached this question by the method of partial hydrolysis. A protein, the products of which on complete hydrolysis are known, is partially hydrolyzed. The products of this partial hydrolysis are separated and each is then hydrolyzed by itself. Thus some notion may be gained of the ways in which the component amino acids are linked. In this fashion Abderhalden[9] obtained from edestin a body yielding glutaminic acid and tryptophane, another yielding glutaminic acid, tryptophane and leucine, and a third yielding tyrosine, glycocoll and leucine. From elastin he obtained *l*-leucyl-*d*-alanine. The isomer of the latter had previously been obtained by Fischer and Abderhalden.[6]

While these studies have not led to the discovery of new amino acids, F. Ehrlich has shown that both normal and isoleucine occur in nature, the latter especially in plants.[10] This discovery grew out of important researches carried out by Ehrlich[1] and H. Pringsheim[2] independently culminating in the proof that amyl alcohol produced by yeast in fermentation was not the product of carbohydrate fermentation at all but of the protein metabolism of the yeast cell. The latter if offered leucine as a source of nitrogen deamidizes it, utilizing the ammonia to build up its own protein and excreting amyl alcohol. The fact that both *n*- and isoleucine occur, accounts for the formation of both *n*- and isoamyl alcohol. Somewhat similar conditions have been demonstrated for the *B. proteus* by Naviasky.[3] Ehrlich[4] was able to use his discovery in splitting racemic amino acids by partial fermentation with yeast in sugar solution. He thus isolated *d*-leucine, *d*-alanine, *l*-valine, *d*-phenylalanine, *d*-serine, and *l*-*a*-aminophenylacetic acid, the latter being new.

---

[1] *Am J. Physiol.*, **23**, 200.

[2] Osborne and Clapp, *Am. J. Physiol*, **20**, 494

[3] Cf. supr.

[4] *Amer. Jr. Physiol.*, **22**, 423.

[5] *Z. physiol. Chem.*, **47**, 458.

[6] *Ber.*, **40**, 3553.

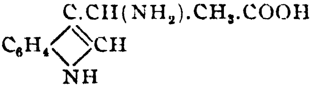
[7] *Z. physiol. Chem.*, **58**, 373.

[8] *Monatsh. Chem.*, **30**, 289.

[9] *Loc. cit.*

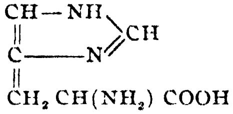
[10] *Ber.*, **40**, 2538.

Among the known substances the constitution of which has been cleared up is tryptophane. It has been shown to be[5]



$$\begin{array}{c} C.CH(NH_2).CH_3.COOH \\ C_6H_4\langle\rangle CH \\ NH \end{array}$$

and the racemic form has been made synthetically. Furthermore Pauly,[6] Knoop and Windaus,[7] and Knoop[8] have proved that the formula of histidine is



$$\begin{array}{l} CH-NH \\ \| \qquad \quad \rangle CH \\ C-\!\!-\!\!-N \\ \| \\ CH_2\,CH(NH_2)\,COOH \end{array}$$

and Windaus and Vogt[9] have made progress in its synthesis. It will be noted that histidine is an imidazole derivative, a fact that is particularly significant if we recall that Pinner long ago showed[10] that an imidazole complex occurs among the alkaloids in pilocarpine. The discovery of the imidazole group in proteins gains further significance from the fact that Knoop and Windaus[11] have found that by the action of ammonia upon glucose imidazole derivatives are formed. E. Friedman[12] cleared up the constitution of adrenaline (epinephrine, suprarenine) and advanced far in its synthesis as did also Stolz. Stolz and Flächer finally succeeded in making *dl*-adrenaline synthetically. The commercial importance of this substance has greatly stimulated studies along these lines, which are recorded mainly in the patent literature. Recently Flächer[13] has succeeded in separating the synthetic product into its *d*- and *l*-components

[1] *Ber.*, 40, 1027.

[2] *Bioch. Z.*, 3, 121.

[3] *Arch. Hyg.*, 66, 209.

[4] *Biochem. Z.*, 8, 438.

[5] Ellinger and Flamand, *Ber.*, 40, 3029.

[6] *Z. physiol. Chem.*, 42, 513.

[7] *Beitrage chem. Physiol. Path.*, 7, 144; 8, 406.

[8] *Ibid.*, 10, 111.

[9] *Ber.*, 40, 3691.

[10] *Ibid.*, 35, 2444.

[11] *Ibid.*, 38, 1166.

[12] *Beitr. chem. Physiol. Path.*, 8, 95.

[13] *Z. physiol. Chem.*, 58, 189.

by means of the acid *d*-tartaric acid salt. Cushny,[1] H. Mayer and Loewi,[2] and Abderhalden and Müller[3] have studied the isomers and have shown that the *l*-adrenaline is the most active; *d*-adrenaline is so much weaker that its activity might possibly be due to contamination with *l*-adrenaline, a striking instance of how slight differences in constitution may condition enormous differences in physiological action. *dl*-Adrenaline is intermediary.

Constitutional studies have, however, not been limited to bodies of unknown conformation. E. Fischer, in order to get easily by synthetic means material for his syntheses of polypeptides, has been driven to devise new methods for the synthesis and the characterization of well known amino acids. In this work he was confronted with the possibility of intramolecular rearrangements such as were first described by Walden. As long as there is a possibility of such rearrangements there can be no certainty that synthetic amino acids actually have the constitution to be expected from the method of preparation. It therefore became necessary to determine the conditions under which these rearrangements take place. The study of a series of amino acids led to the conclusion that this phenomenon is a most complex one, to be understood only on the basis of extensive experimental data[4] which he has since been engaged in supplying. For the present all conclusions as to the constitution of new bodies derived by substitution of the asymmetric carbon must be regarded as provisional.

With the increased ease of obtaining amino acids as the result of these and earlier similar studies by Fischer and his school, it became possible to link together amino acids in the same way in which they occur in proteins. In this way an octadecapeptide of a molecular weight of 1213 was made, the constitution of which is absolutely clear. Still larger molecules might easily be made.[5] These bodies, obtained by condensation of two or more amino acids, and known as polypeptides, were also found naturally. Fischer and Abderhalden[6] found glycyl-*d*-alanine among the products of hydrolysis by acids, while Levene at nearly the same time and independently found glycyl-proline among the products of digestion.[7] This was followed by the discovery by Fischer and Abderhalden[6] of a tetrapeptide which could be salted out with ammonium sulphate like an albumose. Fischer[8] succeeded in making synthetically a tetrapeptide resembling it in every way except that it can not be salted out with ammonium sulphate. It would therefore seem that not merely is tyrosine necessary to give these peptides an albumose character, but it must also occupy a definite position. Thus Fischer's tripeptide, *d*-alanyl-glycyl-*l*-tyrosine, can be salted out by ammonium sulphate,[9] while its isomer glycyl-*d*-alanyl-*l*-tyrosine prepared by Abderhalden and Hirzowski[10] cannot. The preparation of this type of peptide, containing hydroxyamino acids, presents great difficulties because of the sensitiveness of the hydroxyl. Fischer overcame this difficulty by the introduction of a carbomethoxy group into the hydroxyamino acid.[1]

---

[1] *J. Physiol.*, **37**, 130.

[2] *Arch exp. Path. Pharmak.*, **53**, 213

[3] *Zeit. physiol. Chem.*, **58**, 185

[4] *Ber.*, **41**, 2894.

[5] *Ibid.*, **40**, 1754.

[6] *Ibid.*, **40**, 3544.

[7] *J. Exp. Med.*, **8**, 180

[8] *Ber.*, **41**, 850.

[9] *Ibid.*, **40**, 3704.

[10] *Ibid.*, **41**, 2841.

These more purely chemical studies, resulting in a better understanding of the cleavage products of protein, have reawakened interest in the old question as to the possibility of the synthesis of protein in the animal organism. As long ago as 1902 Loewi showed that a dog could be made to retain nitrogen when fed upon carbohydrate and pancreas autolyzed to the disappearance of the biuret reaction. The inferences which should be drawn from this evidence were not accepted at once; but to-day, due to the work of Abderhalden and Rona,[2] Henriques and Hansen,[3] Lüthje[4] and others, it may be regarded as settled that the dog is able to maintain nitrogen equilibrium by means of the biuret-free cleavage products of a single protein or better still of a mixture of proteins. It seems to be immaterial whether the cleavage is carried out by autolytic enzymes already present, or by the addition of peptic or tryptic enzymes, or whether it is carried down to the simplest amino acids. It is probable that a considerable variety of amino acids must be present, which offers an explanation for the well-known fact that gelatin is incapable of replacing the ordinary food proteins, for Kauffmann[5] was able to maintain nitrogenous equilibrium upon a diet containing no ordinary protein but in its stead gelatin, together with the cystine, tyrosine and tryptophane which gelatin lacks. Nitrogen equilibrium can, however, be maintained upon protein cleavage products only when carbohydrates are also fed; not when they are absent and replaced completely by fat,[6] a fact which finds its analogy in plants in the synthesis of asparagine to protein which takes place only in the presence of starch. However, even in the presence of carbohydrate, protein regeneration is impossible from the cleavage products obtained by hydrolysis with strong mineral acids, probably because of secondary decompositions and racemizations. Still more recently Abderhalden, Meszner and Windrath[7] by feeding dogs casein far hydrolyzed with pepsin and trypsin were able not merely to maintain nitrogen equilibrium, but also to cause nitrogen retention. As regards the herbivora we are still in the dark. There is as yet no evidence that they regenerate protein from crystallizable amino acids; but this question has interested investigators less than the problem whether herbivora are able to synthesize protein from the amides which form so important an element of their food and which in some instances (asparagine) are, for herbivora, excellent protein sparers. M. Müller,[8] Völtz,[9] and Lehmann[10] believe they have demonstrated this protein synthesis, while Friedländer,[1] Kellner[2] and others hold the opposite view. Morgen, Berger and Westhausen[3] in studying the effect of amide nitrogen upon milk production conclude that it is not able to replace protein.

---

[1] *Ber*, 41, 2860.

[2] *Z. physiol. Chem.*, 47, 397; 52, 507.

[3] *Ibid*, 49, 114.

[4] *Pflüger's Archiv*, 113, 547.

[5] *Ibid*, 109, 440.

[6] Lüthje, *Ergebnisse der Physiologie* (1908), s. 827.

[7] *Z. physiol. Chem.*, 59, 35.

[8] *Pfluger's Archiv*, 112, 245.

[9] *Ibid.*, 112, 413.

[10] *Ibid.*, 112, 339; 115, 448.

These views have led to endeavors to learn just how far the proteins are split in the gut, and in what form they are absorbed in consequence. Is it necessary for each protein to be split completely into amino acids, or is only a portion of the amino acids removed leaving larger complexes like polypeptides? The most recent evidence speaks for the latter possibility. There is in fact no evidence that all proteins must necessarily be split before they can be utilized; there is much against this view. Fischer and Abderhalden[4] have long since shown that neither tryptic nor peptic digestion, nor both combined, are able to split protein to such an extent that all the polypeptides disappear. In a series of researches Abderhalden and London, Abderhalden, London and Renveelin,[5] Abderhalden, Medigreceanu and London[6] have endeavored to learn just how far digestion proceeds in the different sections of the gut. These researches have not yet been entirely completed, but it has been shown after feeding edestin, casein, and egg albumin, that the amount of material precipitable with phosphotungstic acid rapidly diminishes as the food passes down into the lower sections of the intestines. The amount of tyrosine in this precipitate is very slight even in the upper sections of the intestines, while glutaminic acid is very much more slowly split off. It is present in the phosphotungstic acid precipitate from the contents of the lowest parts. All this is in harmony with the fact long known that some proteins fed to excess may appear in blood and urine in small amounts. It has furthermore long been known that proteins introduced intravenously or parenterally may be utilized, phenomena that have more recently been reinvestigated by Lommel.[7] Freund[8] and Borchardt[9] have endeavored to explain the seeming discrepancy between the fact that proteins introduced parenterally or intravenously are utilized, apparently directly, and the fact that those introduced *per os* are first more or less split. Freund[10] believes that the intervention of the intestines is necessary in order that during hunger protein may be decomposed, while Borchardt[10] was able to show that parenterally introduced elastin albumoses which are easily distinguished from other albumoses, actually accumulate in the intestinal wall. According to this view the conversion of one body protein into another requires the intervention of the intestines, a view in harmony with the theory that protein cleavage is a necessary preliminary to protein synthesis. Thus the view is gaining ground that the intestines are not merely the seat of protein cleavage and subsequent

[1] *Die Landw. Versuchsta.* (1907), s. 283

[2] *Pfluger's Archiv*, **113**, 480.

[3] *Die Landw. Versuchsta.* (1907), 413

[4] *Z. physiol. Chem.*, **39**, 81; **40**, 215.

[5] *Z. physiol Chem*, **58**, 432

[6] *Ibid.*, p. 435.

[7] *Arch. exp. Path Pharm.*, **58**, 50.

[8] *Z. exp. Path. Therap.*, **4**, 1.

[9] *Z. physiol Chem.*, **51**, 506

[10] *Loc. cit.*

absorption of the cleavage products, but also of protein regeneration. The question how far the proteins are regenerated within the intestinal wall still remains open. Older observers, and more recently Freund[1] and Borchardt,[1] were able to demonstrate albumoses and peptones in the blood, whereas Morawitz and Dietschy[2] were unable to do so. Upon the decision of this question hinges very largely Abderhalden's conception of protein metabolism [3] Within the gut the proteins are split more or less. In the intestinal wall protein is regenerated—not the protein of the tissues, but of the blood plasma. From the latter the tissues form their specific proteins.

These ideas give us no notion of the mechanism by which proteins are formed from crystalline material; and of course nothing but surmises can be offered upon this point. Still Taylor[4] and Robertson[5] have shown that their synthesis by enzyme action is possible. Taylor[1] took the pure amino acids obtained from protamine in concentrated solution and allowed trypsin to act upon this mixture. After some months he was able to obtain a small amount of material which had the same physical characteristics as, and the empirical formula of, the original protamine. Whether it was identical or merely isomeric with it was not determined. On the other hand Levene and Van Slyke[6] have brought forward evidence that plastein, supposed to be produced by the action of trypsin upon albumose, may be nothing but albumose and not native protein.

These advances have not been without their influence upon the investigation of pathological protein metabolism. Abderhalden and Samuely,[7] Falta and Langstein,[8] Garrod,[9] Neubauer,[10] and others, have made interesting studies upon the metabolism in alkaptonuria. The latter depicts normal metabolism as follows: The protein molecule is split within the organism mainly into amino and diamino acids. By oxidation and deamidization the amino acids are converted into the corresponding keto acids. The keto acids of the aliphatic series are converted by cleavage of carbon dioxide and oxidation into acids with one less C-atom. Their subsequent oxidation follows known laws. Of the aromatic amino acids tyrosine is first converted into the corresponding keto acid, which is oxidized to the corresponding quinol and then converted into hydroquinonepyrotartaric acid. The latter, after splitting off carbon dioxide, is oxidized to the next lower acid, homogentisinic acid. By further oxidation the benzene ring is opened and acetone bodies appear which are burned to carbon dioxide and water. Phenylalanine is converted either into phenylpyrotartaric acid or into tyrosine and then into *p*-hydroxyphenylpyrotartaric acid. It is then oxidized like tyrosine. In alkaptonuria only the oxidation of tyrosine and phenylalanine is disturbed, proceeding only to homogentisinic acid. The method of oxidation of tryptophane is not known.

---

[1] *Loc cit.*

[2] *Arch. expt. Path. Pharm.*, 54, 88.

[3] Abderhalden, Funk und London: *Z. physiol. Chem.*, 51, 272.

[4] *J. Biol. Chem.*, 5, 381; *Z. physiol. Chem.*, 69, 585.

[5] *J. Biol. Chem.*, 5, 493.

[6] *Biochem. Z.*, 13, 458; 16, 203.

[7] *Z. physiol Chem.*, 46, 193.

[8] *Deut. Arch. klin. Med.*, 81, 250.

[9] *Lancet*, 1908, .

[10] *Deut. Arch. klin. Med.*, 95, 211.

Wolf and Marriott,[1] Wolf and Shaffer,[2] Williams and Wolf,[3] Simon,[4] and Garrod[5] have in part confirmed, in part modified and added to the views of Alsberg and Folin[6] on cystinuria. The view of Loewy and Mayer[7] that more than one form of cystine exists has not been confirmed.[8] It is possible that discrepancies are due to the occurrence of tyrosine in some urinary cystine stones.[9]

While all these advances in protein chemistry, however important, are but continuations and elaborations of older lines of work, this is not so for the chemistry of the fats and lipoids. Their study, which had flagged, has received a powerful stimulus because of the renewed interest in the chemistry of the nervous system; because of the theory advanced by Overton and H Mayer that the lipoids are involved in the mechanism of the action of the indifferent narcotics; because of the view, now pretty general, that the lipoids are an important element of the cell-membrane; and finally because it has been shown that they are an important factor in some of the phenomena of hemolysis and immunochemistry. The upshot of this activity has been, curiously enough, to win posthumous recognition for the work of Thudichum.[10] The majority of the substances isolated by him have to-day a definite status.[11] The animus which seems to have crept into these most difficult studies from the beginning still remains, being concentrated in two discussions. The first involves the chemical unity of protagon. This is maintained by Wilson and Cramer[12] but denied by Rosenheim and Tebb,[13] a confirmation of Lesem and Gies,[14] and a long series of investigators reaching as far back as 1874 (Thudichum) The general drift of opinion seems to be to regard it as a mixture. The second subject of polemic is intimately associated with the protagon question. It concerns the identity of cerebrin, cerebron, pseudocerebrin, and phrenosin. Chiefly concerned in it have been Posner and Gies[15] and Gies[16] maintaining the identity of cerebron and phrenosin, and Thierfelder[17] denying it. It is

[1] *Amer J. Med Science*, **133**, 197

[2] *J Biol. Chem.*, **4**, 439

[3] *Ibid* , **6**, 337.

[4] *Z. physiol. Chem.*, **45**, 357.

[5] *Loc. cit.*

[6] *Amer. J. Physiol.*, **14**, 54.

[7] *Z. physiol. Chem* , **44**, 472.

[8] Fischer and Suzuki, *Z. physiol. Chem* , **45**, 405; Abderhalden, *Ibid.*, **51**, 391 ; Rothera, *J. Physiol.*, **32**, 177

[9] Fischer and Suzuki, *Loc cit*

[10] "Die chemische Konstitution des Gehirns des Menschen und der Tiere." Tübingen, 1901.

[11] Koch, *Am. J. Physiol* , **11**, 303.

[12] *J. Exp. Physiol.*, **1**, 97.

[13] *J. Physiol* , **36**, 1.

[14] *Am. J. Physiol* , **8**, 183.

[15] *J. Biol. Chem* , **1**, 59.

[16] *Ibid.*, **2**, 159.

[17] *Z. physiol. Chem.*, **46**, 518.

probable that they are identical, and incidentally Posner and Gies have also offered evidence for the heterogeneous nature of protagon. It is evident, therefore, that despite the renewed interest in the brain, this, the most difficult field of all biochemistry, still needs a tremendous lot of cultivation. Perhaps the most important fact that has as yet appeared is the existence of highly unsaturated fatty acids in the molecule of some of the brain lipoids. Lecithin, more usually studied in egg-yolk than in the brain, may of course contain oleic acid. A still more unsaturated acid can be obtained from the lipoid kephalin, Thudichum's kephalinic acid, which is so oxidizable that it has not yet been obtained pure.[1] Physiologically the presence of these oxidizable substances in the brain is significant. They help to make brain chemistry complex, a difficulty which is further increased by the probable occurrence of stereoisomers of the commoner acids of which a larger variety is present in the brain than was formerly supposed. Fränkel obtained lauric and myristic acids,[2] while Thudichum's isomer of stearic acid has gained in probability since Kunz-Krause and Massute[3] have actually obtained such an acid from Indian cantharides, probably isomeric with stearic acid: $(C_4H_9)_2.CH(CH_2)_3.CH.CH_3.CH_2CHCH_3.COOH$.

All these findings indicate a great variety and complexity of the brain lipoids. This seems to apply to other tissues as well.[4] Moreover the lipoids seem to differ in different tissues so that specific tissue differences may perhaps in great measure be due to specific lipoids.

The specific nature of many of the lipoids is based not merely upon their isolation and chemical characterization but also upon experimental work in the field of hemolysis and immunity. Gottlieb and Lefmann,[5] and Lefmann,[6] have shown that the toxic substances of red blood corpuscles are probably lipoids because they are soluble in ether and in oil. Lefmann[7] has shown that the lipoids of the corpuscles of the same species of animal are not toxic whereas those of another species of animal may be very toxic. Bang and Forssman have offered similar evidence of the specific nature of the lipoids.[8] Noguchi[9] has shown that many hemolytic substances are merely soaps, while Faust and Tollquist[10] found that many unsaturated fatty acids are powerfully hemolytic. Neuberg[11] has shown that there is some sort of relation between hemolysis and lipolysis, for lipase always accompanies hemolysins. Noguchi[12] has also shown that the lipoids are concerned in bacteriocidal action. v. Liebermann[13] was able to use oleic acid as an immuno-body.

[1] Koch, *Loc. cit.*

[2] *Ergebnisse der Physiologie*, 1909, p. 251.

[3] *Chem. Ztg.*, **31**, 991

[4] Yolk, Fränkel and Boloffio, *Biochem Z*, **9**, 44; Henriques and Hansen, *Skand. Arch. Physiol*, **14**, 390; Stern und Thierfelder, *Z physiol Chem.*, **53**, 370; Oxheart, Erlandsen, *Z. physiol Chem.*, **51**, 71; Liver, Hartley, *J. Physiol.*, **36**, 17; **38**, 353.

[5] *Med. Klinik*, 1907.

[6] *Beiträge chem Physiol Pathol.*, **11**, 255.

[7] *Loc. cit.*

[8] *Beiträge chem. Phys. Path.* Vol. 6.

[9] *Bioch. Z.*, **6**, 327.

[10] *Arch. exp. Path. Pharm.*, **57**, 367.

[11] *Biochem. Z.*, **11**.

[12] *Ibid., Z.*, **6**, 185.

[13] *Biochem. Z.*, **4**.

As one would expect from the discovery that the tissue lipoids occur in considerable variety, the unsaturated fatty acids are not confined to the brain. Leathes[1] and Hartley[2] as well as some of the investigators of tissue lipoids, already mentioned, have shown that fatty acids more unsaturated than oleic acid occur abundantly These are derived no doubt for the greater part from the lipoids but a part probably occur as glycerides.[3] The adipose tissues, however, contain none but the ordinary glycerides. Leathes[2] has therefore been led to the following view:

"It seems therefore that the fat is deposited in the connective tissues unchanged, changes subsequently taking place in it, with the result that it contains more of the unsaturated acid, before it is used in the organs in which it is broken up The unsaturated linkages become more numerous, presumably because it is at these points that the chains of carbon atoms are to break. If we could catch the process at a more advanced stage we should find that some of the unsaturated acids had disappeared, and the mean molecular weight of the acids had diminished. * * * * * We may expect that the fatty acids undergo oxidation step by step * * * * * that an unsaturated linkage is the first move towards this oxidation and probably the formation of a saturated oxyacid the second, the first of these preparatory changes takes place either in the organs where the oxidation is carried out or before it reaches them; but after it leaves the storage places, possibly in the liver."

That fat is transported from the depots to the liver is an old established fact (Lebedeff, Rosenfeld, Leick and Winckler). It may be supposed that this breaking up of the long chains results in such substances as caproic and acetic acids, of which it is known that the organism oxidizes them easily. Dakin's studies[4] upon the course of oxidation of such substances have thrown light upon this phase of intermediary metabolism. Von Furth[5] has described similar changes during the germination of seeds, a lowering of the iodine and acetyl values and the formation of acids of a lower molecular weight. For plants a very similar view has been expressed by Euler.[6] He assumes that hydroxyl groups appear primarily, followed secondarily by a breaking up of the molecule. The smaller cleavage fragments are completely burned, while the larger ones containing hydroxyl groups are utilized in the synthesis of carbohydrate. This is strikingly similar to the opinion expressed by Rosenfeld that fats are completely oxidized in the animal economy only when they become involved in the carbohydrate metabolism.

Schöndorff[7] finds that under special conditions of feeding fat is excreted by dogs through the urine. S. Levites[8] finds that the sodium salts of stearic, palmitic, and oleic acid are absorbed more rapidly than the free acids, and that oleic acid is absorbed more rapidly than palmitic and the latter more rapidly than stearic acid. Von Fürth and D. Schutz[9] obtained the opposite result, for they found sodium oleate and stearate less well absorbed than oleic acid or olive oil.

---

[1] "Problems in Animal Metabolism," p. 107 (1906).

[2] *Loc cit*

[3] Kennaway and Leathes, Lancet, Jan 9, 1909.

[4] *J. Biol Chem.*, **4**, 63, 71, 91, 227.

[5] *Beitrage chem Physiol. Path.*, **4**, 430.

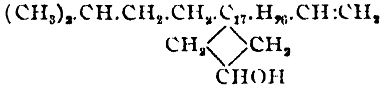
[6] *Z. physiol. Chem.*, **5**, 254.

[7] *Arch. Physiol*, **117**, 291.

[8] *Z. physiol. Chem.*, **53**, 349.

[9] *Beitr. chem. Physiol. u. Path.*, **10**, 462.

The study of the lipoids could hardly fail to stimulate the investigation of cholesterol which so often accompanies them. It has been shown that in plants a large number of different cholesterol occur.[1] The constitution has been investigated by Diels and Abderhalden,[2] by Diels,[3] by Mauthner[4] and by Windaus.[5] The results so far attained may be summed up in the following formula:



$$\begin{array}{c}(CH_3)_2.CH.CH_2.CH_2.C_{17}.H_{26}.CH:CH_2 \\ CH_2\langle\rangle CH_2 \\ CHOH\end{array}$$

From the behavior of cholesterol to ozone Molinari and Fenaroli[6] and Dorée[7] conclude that it contains a second double bond. It is interesting to note that cholesterol contains a five carbon ring which was known only in plants. The theory has been advanced that it is the source of these ring compounds in certain mineral oils. By the researches of C. Engler,[8] M. Rakusin[9] and J. Marcussohn[10] it has been shown that mineral oils owe their optical activity to cholesterol derivatives. C. Neuberg[11] objects to this view. Marcussohn believes these cholesterol compounds to be derived from marine animals, while Walden[12] ascribes them to the sitostearins of plants. Lewkowitsch[13] obtained by distillation of optically active glycerides (Chaulmugra oil) with zinc dust, optically active hydro carbons. In this case the optical activity is not dependent upon cholesterol but upon the configuration of the fatty acids. Neuberg, because of the rarity of such material, slights the experiments.[14]

Our knowledge of the physiological rôle of cholesterol has been increased by Dorée and Gardner, who found it to be a constituent of the cell membrane of the red blood corpuscles. In the bile it is derived from the membranes of destroyed corpuscles. It is to a great extent reabsorbed and used to help in the formation of new cell membranes.[15] It is supposed to be involved in hemolysis, being leached out, with lipoids, by such hemolytic agents as ether, etc., or combining with others such as saponins.[16] The addition of cholesterol often inhibits hemolysis. For hemoly-

[1] Windaus and Hauth, *Ber*, 39, 4378; 40, 3661; F. M. Jager, *Chem. Zentr.* (1907), I, 13, 703, II, 684.

[2] *Ber.*, 36, 3177 (1903)

[3] *Ibid.*, 41, 2597.

[4] *Montash. Chem.*, 30, 635.

[5] *Ber.*, 41, 611, 2558.

[6] *Ibid.*, 41, 2785.

[7] *J. Chem Soc*, 93, 1330; 95, 638.

[8] *Chem. Ztg.* (1906), 711.

[9] *Ibid.* (1906), Nr. 85.

[10] *Ibid.*, 31, 419.

[11] *Bioch Zeit.* (1906), xxx, I, 368.

[12] *Chem. Ztg.* (1906), 1167.

[13] *Ber.*, 40, 4161.

[14] *Ibid.*, 40, 4477.

[15] *Proc. Roy. Soc. B.*, 81, 109.

[16] Dorée, Ellis and Gardner, *Proc. Roy. Soc. B.*, 80, 1908; 81, 1909, p. 505; Choroburo Kusumoto, *Bioch. Z.*, 14, 411 and 416.

sis by saponin Willstätter has found an explanation.[1] He found that when cholesterol in alcoholic solution is treated with digitonin, a typical saponin, a compound is formed which is insoluble in alcohol and can not be decomposed by extraction with ether. It no longer hemolyzes. Sitostearin, stigmastearin, koprostearin and dihydrocholesterol yield similar insoluble crystalline compounds. Cholesteryl esters, which do not hemolyze, do not combine with saponins.

This study of the lipoids has been accompanied by a study of the fat-splitting enzymes. The latter was especially stimulated by the possibility of using these enzymes commercially. Hoyer[2] studied the lipase of the castor bean, as did Taylor.[3] Mastbaum[4] found that of the cola nut, of maize, chestnut, and nutmeg, different from those previously studied. Dietz[5] found that pancreatic lipase not merely saponifies esters, but also synthesizes them, confirmation of older work of Kastle and Loevenhart. The enzyme reaction increases with the concentration, the equilibrium being independent of the latter. It is different from the equilibrium attainable with hydrogen ions, but why is not clear. Interesting is the study made by Dakin[6] of the action of lipase upon the antipodes of asymmetric acid esters. He found that while both esters were saponified, one form was saponified very much more rapidly than its antipode. A still more interesting observation is that of Bredig and Fajans,[7] who found that nicotine used as a catalyzer saponifies *d*-camphoric acid faster than the *l*-acid. We have here relations quite analogous to those of enzyme action, and light is therefore thrown on the "specific" action of enzymes. Not merely asymmetric hydrolysis, but asymmetric enzyme synthesis has been studied. A most interesting asymmetric enzyme synthesis has been discovered by Rosenthaler[8] with emulsin. In emulsin, which is a mixture of enzymes, there is one that accelerates greatly the condensation of benzaldehyde and prussic acid to mandelic nitrile, $C_6H_5CH(OH)CN$, and at the same time causes the radicals tied to the asymmetric carbon atom to arrange themselves in a definite way. This corresponds to *d*-mandelic acid, for on saponification of the nitrile formed, the latter acid with characteristic optical rotation is obtained. In an analogous way most of the aliphatic and aromatic aldehydes in the presence of emulsin combine with prussic acid to form optically active nitriles, while all hydroxyaldehydes and ketones behave differently. Another enzyme has been discovered in yeast. Harden and Young[9] and L. Ivanov[10] showed that in alcoholic fermentation with yeast juice free from yeast cells phosphates are converted into organic phosphorus compounds. Ivanov[11] believes them to be probably phosphoric acid derivatives of a triose, or of dihydroxyacetone, or methylglyoxal. Young[1] believes that they are probably esters of a hexose. He bases his view upon analytical data, cryoscopic determinations, and upon the fact that on saponification they yield fructose in all cases whether formed from phosphate with glucose, or with mannose, or with fructose. This synthesis takes place even when there is no fermentation provided the fermentation products be present. We have here presumably an enzymotic synthesis which perhaps explains the favorable influence of phosphates upon zymase fermentation. The other enzymes of yeast have also received much attention.[2]

---

[1] *Ber.*, 42, 238.

[2] *Z. physiol. Chem.*, 50, 414.

[3] *J. Biol. Chem.*, 2, 87.

[4] *Chem. Revue*, 14, 5.

[5] *Z. physiol. Chem.*, 52, 279.

[6] *J. Physiol.*, 30, 253; 32, 199.

[7] *Ber.*, 41, 752.

[8] *Biochem. Z.*, 14, 238; 17, 257.

[9] *Proc. Chem. Soc.*, 21, 189; *Proc. Roy. Soc. B.*, 77, 405.

[10] *Travaux de la Société des Naturalistes de St. Petersbourg*, 34 (1905); *Z. physiol. Chem.*, 50, 281.

[11] *Loc. cit.*

Rennin (chymosin) and pepsin have also been actively studied. Taylor[3] found that in pyloric cancer the gastric juice has lost its rennin action, though retaining its peptic activity. He therefore concludes that rennin and pepsin are different enzymes. Hammarsten takes a similar view because treatment with weak hydrochloric acid under certain conditions yields a proteolytic but not a coagulating preparation.[4] Petry[5] thinks the proteolytic power of casein due to a new enzyme specific for casein. Van Herwerden agrees with him except that she does not accept the specific nature of the enzyme.[6] Sawjalow[7] and Gewin[8] also think coagulation is a step in the beginning of casein digestion. Van Damm[9] shows on the other hand that chymosin is a proteolytic enzyme and narrows Sawjalow's view down by showing the digestion is due to chymosin itself. He does not agree with Petry, and his evidence points to the identity of casein and pepsin.

The work upon oxidizing ferments has been very great. The whole question is in flux and much of the work is uncritical, due to the unreliability of most oxidase reactions and lack of quantitative methods. Such methods have been offered by v. Czilhary and v. Fürth[10] and by Wichern.[11] Much light is being thrown on this difficult field by the application of work on auto-oxidation.[12] Finally the laccase of *Medicago sativa* has been obtained pure by Euler and Bolin[13] and shown to consist of a mixture of the calcium salts of hydroxy acids, glycolic, glyoxylic, mesoxalic, citric, and malic. The possible significance of such bodies as the first three in respiration is obvious.

Indirectly oxidizing enzymes have also been studied in connection with the purine metabolism. It has been shown by Jones and his collaborators[14] and by Schittenhelm and his collaborators[1] that the various animal organisms contain a variety of enzymes which deamidize and oxidize purines. These authors do not agree upon the distribution and mode of action of these enzymes. Jones holds the view that five distinct enzymes are concerned in these processes: Nuclease, adenase, guanase, xanthooxydase, and uricolase.[2] Nuclease hydrolyzes nucleic acid, forming guanine and adenine; guanase and adenase remove the amino group from these two purines forming xanthine and hypoxanthine; xanthooxydase oxidizes hypoxanthine to xanthine and uric acid. Schittenhelm,[3] and Batelli and Stern, and others have studied the oxidation of uric acid. Wiechowski[4] and Austin[5] deny the force of the evidence for the existence of uric acid enzyme.

---

[1] *Proc. Roy. Soc., B*, 81, 528.

[2] Buchner and Hoffmann, *Biochem. Z.*, 4, 215.

[3] *J. Biol. Chem.*, 5, 399.

[4] *Z. physiol. Chem.*, 56, 18.

[5] *Hofmeister's Beiträge*, 8, 356.

[6] *Z. physiol. Chem.*, 52, 184.

[7] *Ibid.*, 46, 307.

[8] *Ibid.*, 54, 32.

[9] *Ibid.*, 61, 147.

[10] *Beitr. chem. Path. Physiol.*, 10, 358.

[11] *Z. physiol. Chem.*, 57, 365.

[12] Engler and Herzog, *Z. physiol. Chem.*, 59, 327; Manchott, *Verhdl. Phys.-Med. Gesellsch. Würzburg* (1908).

[13] *Z. physik. Chem.*, 69, 187.

[14] *Z. physiol. Chem.*, 44, 1; 48, 571; 60, 180; 61, 395.

An increase in our knowledge of the constitution of nucleic acid has accompanied these advances in our knowledge of the nuclein enzymes. Levene and Jacobs[6] have shown that the pentose of inosinic, guanylic, and yeast nucleic acids is *d*-ribose, at the same time perhaps one of the most important recent contributions to the biochemistry of the carbohydrates. It is the first time this carbohydrate has been found in nature. By partial hydrolysis these authors have thrown much light on the constitution of nucleic acids generally. They believe that nucleic acids are of two types: (*a*) Simple ones, which they term nucleotides, consisting of phosphoric acid, carbohydrate and base (inosinic and guanylic acid); and, (*b*) complex ones (zoo- and phytonucleic acids), which are composed of a number of nucleotides, and which they therefore term polynucleotides. By methods of hydrolysis nucleotides yield two different types of complexes: (*a*) those that consist only of carbohydrate phosphoric acid; (*b*) those that consist only of the basic portion and the carbohydrate which they term nucleosides. Of the former they have prepared *d*-ribose-phosphoric acid from inosinic acid.[7] Of the nucleosides Haiser and Wenzel[8] discovered inosite in meat extract; Levene and Jacobs prepared guanosin from guanylic and yeast nucleic acids, and adenosin from yeast nucleic acid.[9]

Various pigments have been studied, more especially hematin and chlorophyl. Kuster[10] has continued his contributions to the constitution of hematin and bilirubin. The latter exists in several modifications differing in their solubility in chloroform. Qualitatively bilirubin and hematin yield the same oxidation products. Advance in the chemistry of chlorophyl is hampered by confusion in the nomenclature, as is well brought out in a discussion between Marchlewski and Willstätter.[11] The former

---

[1] *Z. physiol. Chem.*, 62, 100, 63, 248; *Zentralbl ges. Physiol. Path. Stoffw.* (1918), No. 19, etc.

[2] *Ibid.*, 61, 399.

[3] *Z. physiol. Chem.*, 45, 121.

[4] *Arch. exp. Path. Pharm.*, 60, 185.

[5] *J. Med. Res.*, 16, 71.

[6] *Ber.*, 42, 335, 1198, 2703.

[7] *Ibid.*, 41, 2703.

[8] *Monatsh. Chem.*, 29, 157.

[9] *Ber.*, 42, 2469, 2474, 2703.

[10] *Z. physiol. Chem.*, 59, 63.

[11] *Chem.-Ztg.*, 33, 674, 871.

Under the same conditions xanthophyl would be more equally divided between the two solvents. Xanthophyl is $C_{40}H_{56}O_2$. Like carotin, it is strongly unsaturated, and absorbs oxygen from the air at ordinary temperatures.

The physiological significance of carotin and xanthophyl remains in doubt. Carotin may act as a carrier of oxygen. Xanthophyl, however, is not passed over in the spontaneous oxidation of carotin in the air, as is shown by the fact that xanthophyl will absorb 36.5 per cent. of its weight of oxygen, but carotin only 34.2 per cent.

V. Willstätter and Pfannenstiel[1] have investigated the remarkable series of transformations which take place on heating chlorophyllin with alcoholic potash. The first change occurs at the temperature of the water bath, in the assumption by the green solution of a strong fluorescence. At 140° the green substance breaks down with the formation of a crystalline product, which is blue with an intense red fluorescence. Finally at about 200° a deep red product is obtained. The products at each stage of the decomposition are mixtures of closely related compounds of similar color. All are magnesium compounds. Those of the first stage, green in color, are the chlorophyllins, those of the second stage, blue, glaucophyllins, and those of the third stage, red, rhodophyllins. One of the latter was prepared for investigation by heating chlorophyllin and potassium hydroxide in a silver beaker in an autoclave. Only one compound was thrown down when the reaction mixture was treated with water. Other related compounds remained in solution. The precipitate was purified by solution in ether and extraction with very dilute ammonia. It was found that the reaction between chlorophyllin and potassium hydroxide could not be carried on in sealed tubes of Jena glass because of the replacement of magnesium by zinc, derived from the glass. An identical rhodophyllin was prepared from *Chlorophyceae*, *Musci*, *Filices*, *Equisetum*, *Gramineae*, *Urticaceae* and *Platanus*, from which it was concluded that magnesium is an essential constituent of the chlorophyl of all plants. The formula which accords best with the analyses of samples of rhodophyllin prepared by various methods is $C_{33}H_{34}O_4N_4Mg$, but the data are hardly exact enough to exclude from consideration the formulas $C_{33}H_{36}O_4N_4Mg$, $C_{32}H_{34}O_4N_4Mg$, and $C_{34}H_{36}O_4N_4Mg$. In any case the compound is strikingly similar to hematin. By the action of acids, the magnesium atom is split from rhodophyllin with formation of a difficultly soluble crystalline derivative of red color, which accords in composition with the mesoporphyrin of Nencki and Zaleski, but is not identical with it. The authors give it the name alloporphyrin, and consider that it is derived from rhodophyllin by the substitution for magnesium (which is probably linked to N) of two hydrogen atoms. The metallic atom is considered to be in complex combination with basic groups of the molecule, in order to account for such color phenomena in the chlorophyl and hemin groups as are conditioned by the entrance of a metal into the compound.

VI. In a paper by Willstätter and Benz[2] the work of Borodin and of Monteverde on crystallized chlorophyl is reviewed and greatly amplified. The work of these students has heretofore hardly received due attention from chemists. The technique of Borodin has been improved so that yields of 2 grams of crystallized chlorophyl per kilogram of dry leaves have been obtained. The process, in essentials, consists of extraction with alcohol, transfer of the chlorophyl to ether, removal of emulsifying substances by shaking with talc, and of other impurities by shaking with water, and, finally, concentration on the water bath to the point of crystallization. The crystals were washed with small quantities of ether, to remove mother liquor, and then recrystallized from ether. The compound thus obtained would seem, from its spectrum, color, and indifference to dilute acids and alkalies to be an unaltered chlorophyl. It is by no means identical, however, with the greater part of the chlorophyl of even the plants from which it is obtained in greatest quantity, for it yields no phytol on hydrolysis, as does ordinary amorphous chlorophyl. It seems that all plants contain amorphous chlorophyl, but only certain ones (190 species out of 776 examined by Borodin) contain, in addition, crystalline chlorophyl. This would explain the varying yields of phytol from different samples of chlorophyl, and also the variation in composition of phaeophytin from different plants, for the compound from crystalline chlorophyl which is analogous to phaeophytin, namely phaeophorbin, probably often occurs as an impurity of phaeophytin when this substance is prepared from the total chlorophyl of plants which contain crystalline chlorophyl.

---

[1] *Ann.*, 358 205–65 (1908).

[2] *Ibid.*, 358, 267–87 (1908).

Crystalline chlorophyl prepared from *Galeopsis* gave 5.64 per cent. of ash-- pure magnesium oxide. On a basis of one atom of magnesium to the molecule, this would correspond to a molecular weight of 716, and the formula $C_{38}H_{42}N_4Mg$. As in the case of amorphous chlorophyl, the magnesium atom is readily split off by dilute acids.

A substance for which as for cholesterol no physiological function was known, inosite, has been the subject of investigation. W. Windisch[1] has shown that a mother substance for it is phytin, confirming older observations of Jordan, Hart and Patten[2] while Mayer[3] has shown that when inosite is fed in large doses to rabbits fermentation lactic acid appears in the urine. Concerning lactic acid we have learned much through Fletcher and Hopkins.[4] They have shown that our methods for its determination in muscle are very unreliable. Though they have thrown much light upon the genesis of this acid they have not endeavored to discover its precursors in the animal body. Herzog and Hörth[5] have studied the stereochemistry of lactic acid fermentation; and have found that different bacteria acting upon different sugars usually form an acid, which is a mixture of active and inactive acid.

There have been other advances in the biochemistry of lactic acid, particularly in regard to its rôle in the intermediary metabolism in relation to both the carbohydrates and the amino acids. While these researches ought, strictly speaking, to be included in this review, to do so would lead us into the field of intermediary metabolism in which there have been some notable advances. To treat them adequately would require more

[1] *Jahrb. Vers. u. Lehranstalt für Brauerei*, **10**, 57.

[2] *Am. J. Physiol.*, **16**, 288; **17**, 76.

[3] *Bioch. Z.*, **2**, 393; **9**, 533.

[4] *J. Physiol.*, **35**, 347.

[5] *Z. physiol. Chem.*, **60**, 131.

space than is at my disposal, so that a review of these advances as well as those very important ones resulting from the application of physical chemistry to biology must be postponed to some future date, at which time the many errors of omission of which I am conscious may, I hope, be amended.

WASHINGTON, D C

NEW BOOKS.

Einführung in die Chemie. Ein Lehrbuch für höhere Lehranstalten und zum Selbstunterricht. By WILHELM OSTWALD, Stuttgart, 1910: Franckh'sche Verlagshandlung. pp. 238; 74 illustrations in the text. Cloth, 3 Marks net.

In this textbook it is the main object of Professor Ostwald to educate the student to "chemical thinking," to supply a basis for chemical understanding and to deepen the logical analysis of the chemical phenomena. Contrary to the methods pursued in most other textbooks, Professor Ostwald prefers to give only the data absolutely necessary for the understanding of the scientific consequences and to describe only the phenomena absolutely essential for grasping the real educational value of chemistry.

This is quite a new departure, since in most of the textbooks such a lot of material is presented, that the students get the impression that by learning the contents of the respective book he will know all about chemistry. Ostwald's book, on the contrary, incites to further thinking and impresses the student with what may be called scientific modesty. The first five chapters contain a discussion of matter, mixtures, physical transformations, solutions and chemical processes. Chapters 6 to 13 describe the metallic and non-metallic elements and compounds in a clear and concise, *i. e.*, really Ostwaldian manner. The book will prove as useful to the teacher as to the student.

OSKAR NAGEL.

Introduction to Physical Chemistry. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. New York: The Macmillan Co 1910. xv + 279 pp. Price, $1.60 net.

So far as we know, this is the most recent work from Prof. Jones' pen. Using 'recent' as he uses it, however, we could not feel secure in this statement. "Quite recently" on p. 47 refers to 1895, and on p. 113 to 1899. The epoch of writing may, however, perhaps be fixed from internal evidence for (p. 136) 'Berthelot's experimental work has continued up to the present' and "van't Hoff's paper on the subject of solid solutions appeared about eleven years ago." The purpose of the book is sufficiently obvious from the title. Symptoms of adaptations from the author's larger works appear at times rather prominently. Thus we find, on p. 67, two liquids becoming miscible in all proportions, "as we have just seen." We have not, however, seen it in the present volume.

Again, we are told, on p. 26, that the author will call the temperature coefficient of gases "B." Having mentally agreed to this and assimilated the significance of "B," we read on in expectation. "B," however, fails to put in any further appearance. But we must not be too disappointed, for this is an optimistic book We find the author taking a characteristically optimistic view of the agreement of results "found" with those calculated by theory on p. 61. Here we notice divergencies of 10 per cent. and more in the square of a quantity calculated from measurements of absolute boiling point and of densities at 0°, both of which quantities are customarily measured with concordance of well within half a per cent. by different observers. The agreement is, nevertheless, stated to be "almost within the limits of experimental error." Optimism is a good fault, and is well in keeping with the vigor and freshness that characterizes much of the exposition. No book is without its *corrigenda,* and the following are among points that might perhaps receive attention. For the atomic weight of radium read 226 4, not 225 (p. 11), and 226 7, not 227.7 (p. 151). These are misquoted from the sources given. This element suffers again in being omitted from the table of the periodic law (p. 13). Mass is "the only property of substances that remains unchanged in chemical reaction" (p. 1). Surely orthophosphoric acid can be titrated with phenolphthalein as indicator (p. 112). As far as one can gather from p. 129, the equivalent concentration of hydrogen ion in pure water at 18° is 0 68. On p. 196, water is the strongest dissociant known; but, on p. 194, water stood second to liquid hydrocyanic acid. "Compounds of uranium when exposed to light" emit radiation—is true but perhaps misleading, while "this property is possessed by metallic uranium to from three to four times the extent that it is manifested by the salts" seems to miss the main point of interest. "The definition of an atom as an individual particle of matter shows that fractions of atoms cannot exist" (p. 8). "When barium sulphate and sodium carbonate were pressed together and the pressure removed, the transformation continued, and in seven days amounted to from 73 to 80 per cent." The "73 to 80" is circumstantial, and adds realism; but how thick were the layers? Socratic method is antiquated and slow, else many a beginner might ask ingenuously, "What is intrinsic energy?" (p. 133). Nowadays, one must hurry on and catch the meaning subconsciously as the discussion proceeds.

It is probably difficult for the author to view his subject continuously from the introductory level; and, in writing, it must be tiresome to recall the precise state of ignorance of his reader. Perhaps for this reason we find, for example, Ostwald's dilution law, the isohydric principle, etc., discussed before chemical equilibrium; the theory of indicators before hydrolytic dissociation, etc. There are no forward references. The beginner will doubtless be willing to admit his own obtuseness, but he will be disconcerted.

The book is very free from typographical errors and is, of course, excellently produced. There are 31 efficient diagrams and figures in the text. Though the pedagogy is a weak feature, the style has a refreshing air of activity and modernness, while the matter selected is generally accurate and always interesting. We feel certain, however, that this is not yet the ideal "Introduction to Physical Chemistry." Let the Quest continue. ALAN W. C. MENZIES.

Analyse der Silikat– und Karbonat Gesteine. Von W. F. HILLEBRAND. Deutsche Ausgabe von ERNST WILKE-DORFURT. Leipzig: von Wilhelm Engelmann, 1910.

This volume in its German dress contains numerous additions made by its author to previous editions. The fact that German students have recognized its merits and want it in their own language reflects great honor upon its author. Years ago, within the knowledge of some of us, the Fatherland was the seat of most thorough training in mineral analysis. To-day, however, as evidenced by the rich fund of reliable information in this special publication and in other similar publications, America may justly lay claim to this position.

The careful perusal of its pages proved most refreshing to the reviewer, and if he may be allowed a word of advice to students of chemistry, it would be: Study the contents of this book; put to test the methods and experiences therein described. A vast fund of new knowledge will be the reward, a deeper respect for analytical methods and their significance and value will be engendered, while the feeling of contempt so frequently manifested for the work of the mineral analyst will absolutely disappear, and a wider and wholesomer view of the whole field of chemical science will result. Teachers of more advanced students in analysis will realize the greatest pleasure and profit in the consideration of the many topics of this volume in their seminars. EDGAR F. SMITH.

Das Radium und die Farben. PROFESSOR DR. C. DÖLTER, Vorstand des Mineralogischen Institutes der Universität Wien. Verlag von Theodor Steinkopf, Dresden. 1910. pp. 133. Preis, geb. M. 5.

The discovery of radium and a recognition of the complex influences of its several forms of energy have aroused unusual interest for several reasons, but mainly, because, first, radium salts, in their decomposition produce canal and cathode (magneto- or electro-magneto-deflectable) and gamma (Röntgen) rays, exert specific, analytic and synthetic influences, physical, chemical and physiological, which might in a large sense be grouped under the head of chemical; second, when all that is positively known of these influences is applied to the world's history, petrographical and geological, a revision of previous ideas of changes that have taken place and calculations as to the age of the earth have become necessary.

The author has had unusual facilities in Vienna for the study of the many and varied changes produced through the influence of radioactivity. He has taken advantage of them. The book presents the results of his elaborate investigation. It is filled with meat and cannot fail to be of interest to mineralogists, geologists and those chemists who desire further information as to the influence of these complex rays upon matter. It has a good index. CHAS. BASKERVILLE.

The Simple Carbohydrates and the Glucosides. By E. FRANKLAND ARMSTRONG. (Monographs on Biochemistry Series) 112 pages. Longmans, Green & Company. Price, $1.20 net.

This short monograph by Dr. Armstrong, an English investigator of the first rank in carbohydrate chemistry, is a well-written summary of the advances of the last fifteen years in the chemistry of the sugars. Naturally it is impossible to describe these advances in a manner that is satisfactory to an inquiring reader in the space of 112 pages, and it is to be hoped that later editions will be more inclusive. But the monograph is a good beginning and should be widely read by chemists and biologists. To understand the chemical or biological actions of the sugars it is essential to have a clear knowledge of their mutarotation and Dr. Armstrong's book furnishes a good description of this phenomenon. A valuable eighteen-page bibliography is appended. On page 47 the discovery of β-lactose, which was made by E. O Erdmann, is credited to C. Tanret. The discovery that the mutarotation of glucose is a balanced reaction is ascribed on page 8 to Lowry; the reviewer believes that he made the same discovery in the case of lactose in the year preceding Lowry's publication, and that his priority in the discovery of the cause of the mutarotation reaction has been recognized in such a standard work as Nernst's "Theoretische Chemie." Dr. Lowry and he worked independently, the former on glucose, the latter on lactose. C. S. HUDSON.

A Course in Inorganic Chemistry for Colleges. BY LYMAN C. NEWELL, PH.D (Johns Hopkins), Professor of Chemistry, Boston University. Published by D C. Heath and Company, Boston. pp. x + 594. Price, $2 00

This is practically a new and enlarged edition of the author's well-known Descriptive Chemistry. A chapter on Solutions has been added and the chapters on Silicon-Boron and Chromium-Manganese have been enlarged and divided into two separate chapters. While the main portions of the text are identical with the Descriptive Chemistry, yet considerable new material has been added and the subject brought up to date. In a few cases the order of the chapters has been changed. The questions at the end of the chapters have been omitted, but the lists of problems remain. The book is conservatively modern in spirit and is deserving the same cordial recognition given the author's former work.

WILLIAM MCPHERSON.

Outline of Bacteriology (Technical and Agricultural). BY DAVID ELLIS. Longmans, Green & Co , 1909 pp. xii, 262 Price, $2 50

Dr. Ellis, of the Glasgow Technical College, has attempted to write "an introduction to bacteriology in all its branches, though more attention has been bestowed on that aspect of the subject which is of most interest to students of technical and agricultural bacteriology." The plan of his book is an excellent one. There is great need for text-books of bacteriology which shall develop the broader biological facts of the science, without undue emphasis on the details of its application to medicine. It requires, however, an unusual grasp of the subject, a strong sense of proportion, and some literary skill to produce a book of this type. Fischer in the Vorlesungen uber Bacterien has succeeded in doing it: but his admirable volume stands practically alone. The present author gives less of a philosophical treatment of fundamental questions, than a series of more or less independent facts such as make up the bulk of so many books on bacteriology and hygiene. For example in the chapter on sterilization, thirty-three different chemical disinfectants are discussed in detail, including such substances as nitrogen dioxide, butyric acid, camphor and coffee infusion. Dr. Ellis gives his well known views about motility and spore formation among the cocci as established facts without pointing out that they are still in the controversial stage. Here and there are statements of a somewhat superficial character which are likely to prove misleading. The industrial and agricultural chapters, modeled pretty closely after Lafar, are freest from such defects, and the medical and sanitary sections are most prone to them. Thus it is stated that the same species of bacillus causes tuberculosis in man and in cattle (p. 120), and that infection in tuberculosis takes place almost exclusively through the air (121). The colon bacillus is introduced as follows: "There is great similarity between *B. typhosus and Bacillus coli communis*, an organism which is very common in sewage, and which is strongly suspected of being the cause of epidemic diarrhoea, though positive proof is still wanting." Altogether the book is not a sufficiently scholarly work to form a very valuable contribution to the subject. C.-E. A. WINSLOW.

RECENT PUBLICATIONS.

ABDERHALDEN, E.: **Handbuch der biochemischen Arbeitsmethoden.** 11 Bd. 2 Hälfte. Wien: Urban & Schwarzenberg. 24 M.

ALLEN, A. H. **Commercial Organic Analysis.** Fourth edition, Volume I, edited by H. Leffmann and W. A. Davis. Philadelphia: P. Blakiston's Son & Co. $5.00.

ALTMAYER, V.: **Ueber das Methangleichgewicht, die Beziehungen zwischen Nickel und Wasserstoff und einige Methansynthesen mit Calciumhydrür.** München: R. Oldenbourg.

BASKERVILLE, C.: **General Inorganic Chemistry.** Boston: Heath. $1.50.

Baskerville, C., and Curtis, R. W.: **Laboratory Exercises in Inorganic Chemistry.** Boston: Heath. $0.40.

Biedermann, Dr. R.: **Chemiker-Kalendar 1910 Hilfsbuch für Chemiker, Physiker, Mineralogen, Industrielle, Pharmazeuten, Hüttenmänner.** Zwei Teile 31 Jahrgang. Berlin: J. Springer.

Bottler, Max.: **Modern Bleaching Agents and Detergents.** London. Scott & Greenwood. 8°, 176 pp., 5 s.

Byrom, T. H., and Christopher, J. E: **Modern Coking Practice; Including the Analysis of Materials and Products.** Lockwood 8°, 168 pp., 8 s 6 d.

Duparc, L., et Basadonna, M **Manuel théorique et pratique d'analyse volumetrique.** Genf: Libraire Kundig. 8°, 7 Fr

Ellis, D.. **Outlines of Bacteriology** (technical and agricultural) New York: Longmans, Green & Co $2.50

Flamand, J: **La Chimie et la Bactériologie du Brasseur.** Hannut. L Flamand-Godfrin. 8°, 15 Fr.

Frick, J: **Physikalische Technik oder Anleitung zu Experimental-vorträgen, sowie zur Selbstherstellung einfacher Demonstrationsapparate.** 7 Aufl. von O. Lehmann. Braunschweig: F. Vieweg & Sohn.

Gajdeczka, J.: **Lernstoff aus der Physik und Chemie für Lehramtskandidaten.** Wien. Franz Deuticke 306 s., 4.50 M.

Grebe: **Spektroskopie.** Leipzig. B. G. Teubner. 1.25 M.

Greer, W. J.: **Industrial Diseases and Accidents.** Bristol: J. Arrowsmith. 8°, 7 s., 7 d.

Hauberrisser, G.: **Wie erlangt man brillante Negative und schöne Abdrucke.** 15 Aufl. Leipzig: E. Liesegang's Verlag, M. Eger. 1.25 M.

Henle, F. W.: **Anleitung zur organischen Elementaranalyse.** Rev. von Dr. K. Pfister Munchen: M. Riegersche. 8, 40 s., 2 M.

Hempel, H.: **Ueber Gasöle und Oelgas.** München: R. Oldenbourg.

Heuser, E: **Ueber Oxalmalonsäureester.** Greifswald: Hans Adler.

Kahlenberg, L.: **Laboratory Exercises in General Chemistry.** Second edition. Madison, Wis.: L. Kahlenberg. $0.90

Klar, M.: **Technologie der Holzverkohlung.** 2 Aufl. Berlin: J. Springer. 11 M.

Klein, J. H.: **Ueber Vorkommen und Herkunft des Inosit im Tierkörper.** Hildesheim: A. Lax. 1.50 M.

Knecht, E.: **A Manual of Dyeing.** 2 vols., second edition. C. Griffin. 8°, 916 pp., 45 s.

König, J.: **Chemie der menschlichen Nahrungs- und Genussmittel.** 3 Bd., 1 Teil. **Allgemeine Untersuchungsverfahren.** 4 Aufl. Berlin: J. Springer. 26 M.

Küspert, Fr.: **Lehrgang der Chemie und Mineralogie für höhere Schulen.** 2 Aufl. Nürnberg. C. Kochs. 8°, 4.90 M.

Le Blanc, M.: **Die elektromotorischen Kräfte der Polarisation und ihre Messung mit Hilfe des Aszillographen.** Halle a/S: W. Knapp. 3 M.

Leeds, F. H., and Butterfield, W. J. A.: **Acetylene: The Principles of Its Generation and Use.** Second edition. Griffin: 8°, 408 pp., 8 s., 6 d.

Loock: **Chemie und Photographie bei Kriminalforschungen.** Düsseldorf: Fr. Dietz. 3 M.

Lunge, G., und Berl, E.: **Chemisch-technische Untersuchungsmethoden.** 1 Bd. 6 Aufl. Berlin: J. Springer. 20.50 M.

MacEwen, H. A.: **Food Inspection. A Practical Handbook.** Blackie: 8°, 264 pp., 5 s.

Mann, H.: **Die moderne Parfümerie.** 2nd. Aufl. Augsburg: Verlag für chemische Industrie. 8°, 559 s, 12 M.

McClung, R. K.: **Conduction of Electricity through Gases, and Radioactivity; a Textbook with Experiments.** Philadelphia: P. Blakiston's Son & Co. $1.50.

Meigen, Dr. W.: **Uebungsbeispiele zur quantitativen Analyse.** Freiburg i/Br: Speyer und Kaerner. 8°, 60 s., 2 M.

Morden, G. W.: **Die Stickoxybildung aus Luft mit Hilfe einer Gleichstromentladung niedriger Spannung unter vermindertem Druck.** Karlsruhe: G. Braunsche.

Norman, G. M.: **Systematic Practical Organic Chemistry.** Second edition. Clive: 8°, 104 pp, 1 s., 6 d.

Normandy, F: **A Practical Manual on Sea Water Distillation.** London: Griffin & Co. 8°, 6 s.

Oppenheimer, C.: **Handbuch der Biochemie des Menschen und der Tiere.** 11 Bd. 2 Hälfte: **Biochemie der Gewebe und Organe.** Jena: G. Fischer. 8°, 392 s, 16 M.

Ostwald, W.: **Die Entwicklung der Elektrochemie in gemeinverständlicher Darstellung.** Leipzig: J. A. Barth. 208 s., 5.60 M.

Passon, M.: **Kleines Handwörterbuch der Agrikulturchemie.** 2 Teile. Leipzig: W. Engelmann. 8°, 454 u. 415 s., 25 M.

Piccard, J. F.: **Ueber Konstitution und Farbe der Chinonimine.** Zurich: E. Speidel. 8°, 111 s., 2 M.

Prag, E.: **A Course in Dyeing for Garment Dyers.** Phila.: Modern Dyer and Cleaner Pub. Co. $5.00.

Remsen, I.: **An Introduction to the Study of Compounds of Carbon.** Boston: Heath. $1.20.

Richards, R. H.: **Text-Book of Ore Dressing.** New York: McGraw Hill Book Co. $5.00.

Rimbach, E.: **Chemisches Praktikum für Mediziner.** 2 Aufl. Bonn: F. Cohen. 4 M.

Robertson, T. B.: **The Proteins.** Berkeley, Cal., University of California. $1.00.

Routala, F. O.: **Ueber die Bildung der Napthene im Erdöl.** Karlruhe: G. Braunsche.

Rothschild, M.: **Ueber Synthesen ringförmiger Verbindungen mittels Dipropylmalonylchlorids und Succinylchlorids.** Hildescheim: August Lax. 2 M.

Sexton, A. H.: **Fuel and Refractory Materials.** New edition. Blackie: 8°, 364 pp., 5 s.

Simon, Dr. O.: **Laboratoriumsbuch für die Industrie der Riechstoffe.** Halle a/S: W. Knapp. 3 M.

Sudborough, J. J., and Campbell, J. T.: **Practical Organic Chemistry.** New York: D. Van Nostrand. $2.00.

Syllwasschy, E.: **Die Giftprüfung und die Konzession zum Handel mit Giften.** 2 Aufl. Berlin: A. L. Hermann. 128 s., 1.60 M.

VOL. XXXII. JUNE, 1910. No. 6.

THE JOURNAL

OF THE

American Chemical Society

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

HALIDES OF TANTALUM.[1]

BY WALTER K. VAN HAAGEN.

Received April 4, 1910.

The chloride alone of all the possible halides of tantalum has received more than passing attention. A bromide has been recorded but the iodide is absent from our literature. H. Rose[2] claimed to have obtained the bromide by strongly igniting a mixture of tantalic oxide and carbon in a current of carbon dioxide laden with bromine vapor. He failed to give any analytical results. He surmised that his product was the bromide. Moissan believed it was produced upon heating tantalum metal in a stream of bromine vapor.

With pure materials the conditions essential for the satisfactory preparation of tantalum pentabromide may be briefly summarized:

1. Tantalic oxide, previously strongly ignited, should be intimately mixed with an excess of pure carbon, an equal weight of the latter being a convenient and quite sufficient amount. Starch carbon answers well but it usually leaves an appreciable ash, hence pure sugar carbon is preferable. The excess of carbon indicated makes the mass sufficiently permeable to the bromine.

2. Air should be completely expelled. Raise the charge to a full red heat in a current of carbon dioxide to remove the last traces of moisture.

3. Phosphorus pentoxide is essential as the final drying agent for the carbon dioxide.

4. A high temperature must be maintained during the passage of the bromine, otherwise nearly all of it will escape unchanged.

---

[1] An abstract from the author's doctoral thesis (190).

[2] *Pogg. Ann.*, 99, 87 (1856).

5. The resulting pentabromide should be fused from time to time in order that the combustion tube may not be obstructed.

It is easy to get a yield of about 70 per cent. of the theory.

The product from the above procedure was resublimed in an atmosphere of carbon dioxide. Upon analysis it showed:

				Theory.
Ta =	32.21	32.03	31.79	31.39
Br =	68.70	68.68	68.38	68.61

Tantalum pentabromide consists of yellow, elongated lamellae, curving or clinging to the tube in beautiful arborescent forms resembling frost flowers. They fuse easily to a transparent, ruby colored liquid. Their color is suggestive of that of potassium bichromate. They may be sublimed without melting. The vapor of the bromide is yellow in color, somewhat resembling that of chlorine. The bromide melts at about 240° and begins to boil at 320°. It fumes strongly in the air. It dissolves rapidly in absolute methyl or ethyl alcohol, forming at first an amber-yellow colored liquid which soon becomes colorless. Usually, the heat generated causes the alcohol to boil. These reactions certainly point to tantalic esters. Anhydrous ethyl bromide is an interesting solvent for tantalum pentabromide. When the latter is brought into this liquid heat is evolved and a reddish colored solution results. If the latter be cooled in water or evaporated in a vacuum desiccator golden yellow colored crystals separate. The solution fumes strongly in the air.

Tantalum pentabromide may be sublimed in an atmosphere of hydrogen. This is possible at a temperature just sufficient for the sublimation. At more elevated temperatures a partial reduction to the metallic state occurs. If a lower bromide of tantalum should exist such a compound would not be unlikely to appear at some stage during the reduction of the pentabromide in hydrogen. At first there seemed no evidence of this. At times, however, the sublimate appeared to be different. Indeed, it had been noticed that toward the posterior end of the tube, *i. e.*, beyond the metallic deposit, there was a slight greenish, partly almost black film. It dissolved in water with an intense green color, and in methyl and ethyl alcohol with the same color. Its analysis indicated a tantalum tribromide, but Chapin, in this Laboratory, has since demonstrated that it is not this, but that it is in reality a bromo-tantalum bromide $(Ta_6Br_{12})Br_2$.[1]

An oxybromide of tantalum was not observed.

Efforts were made both by Rose[2] and by Moissan[3] to obtain an iodide of tantalum but without avail. So the query presented itself: is it not possible to transpose tantalum bromide by means of a suitable iodide? Silver iodide suggested itself for this purpose. Accordingly tantalum pentabromide was distilled through a column of granular, well-dried silver iodide in a current of carbon dioxide. A brown sublimate resulted. It contained considerable free iodine, which was carefully expelled and the residue analyzed. This analysis indicated a pentabromide with unmistakable evidences of combined iodine. How could there be free iodine unless there had been a reduction of the bromide?

---

[1] W. H. Chapin, THIS JOURNAL, 32, 323.

[2] *Pogg. Ann.*, 99, 593 (1856).

[3] *Compt. Rend.*, 134, 211–215.

Finally it was found that the potassium iodide used in the preparation of the silver iodide contained some iodate. Most likely then the reaction had proceeded as follows:

$$7TaBr_5 + 5AgIO_3 = TaI_5 + 3Ta_2O_5 + 5AgBr + 15Br_2.$$

The liberated bromine set free iodine from the silver iodide and probably from the tantalum iodide, allowing only a small amount of the latter to escape, while by far the greater portion of the bromide distilled over unchanged. This view is further supported by the fact that iodine separates when tantalum pentabromide is distilled through a layer of potassium iodate.

The next thought was to try hydrogen iodide. Accordingly tantalum pentabromide was slowly distilled in a steady stream of anhydrous hydriodic acid gas. Soon the reddish color of the bromide changed to brown, while the escape of hydrobromic acid, together with the excess of the hydriodic acid, could be proved at the exit of the tube. Further an analysis of the dark brown product showed that only one-third of the bromide had been converted into an iodide. Therefore the experiment was repeated, about three grams of the pentabromide being distilled as slowly as possible in a brisk current of hydrogen iodide for about four hours. The product was brownish black in color and showed much iodine. Its tantalum content was found to be 22.98 instead of 22.37 per cent. as required by TaI_5. The remainder of the preparation was subjected to another distillation in hydrogen iodide and analyzed with these results:

	Per cent.	Per cent.
Ta	22.62	22.51
I	77.27	77.35

The required percentage of iodine for the pentaiodide is 77.63. These results prove the formation of an iodide, TaI_5. It sublimes in dark, nearly black lamellae, bearing a remote resemblance to iodine crystals. It fuses to a dark brown liquid. Its vapor is like that of bromine. It may be distilled in a current of carbon dioxide without the separation of iodine. It resembles the bromide in its deportment toward moist air and water. An intermediate oxyiodide was never observed.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 47.]

THE POTENTIAL OF THE THALLIUM ELECTRODE.

BY GILBERT N. LEWIS AND CARL L. VON ENDE.

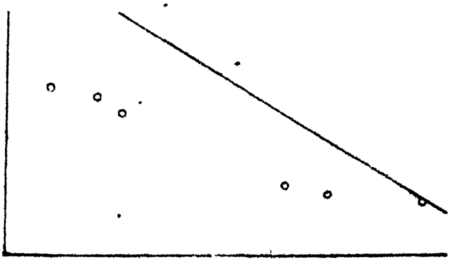
Received March 25, 1910.

The first determination of the electrode potential of thallium was made by Neumann[1] who obtained the following values:

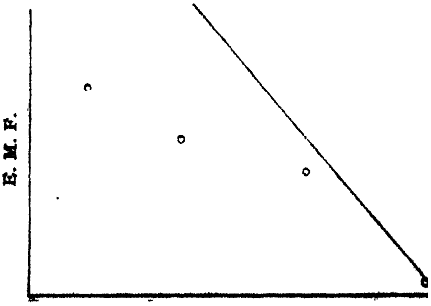
			Volt.
Tl, Tl_2SO_4	(saturated),	N. E.;[2]	$E = +0.674$
Tl, $TlNO_3$	(saturated),	N. E.;	$E = +0.671$
Tl, TlCl	(saturated),	N. E.;	$E = +0.711$
Tl, TlA	(0.1 N),	N. E.;	$E = +0.677$
Tl, TlA	(0.02N),	N. E.;	$E = +0.705$
Tl, TlA	(0.01N),	N. E.;	$E = +0.715$

The last three values are averages obtained from the study of 23 thallous salts, chiefly of organic acids, at the three concentrations given. Neumann believed his results to be entirely reproducible. In fact he found the potential of thallium in the twenty-three salts at hundredth-normal concentration to be the same within one millivolt. This agreement must have been purely accidental for we shall see that all of Neumann's measurements of the thallium potential were attended by a very large error of entirely fortuitous character.

The doubtful character of Neumann's determinations is apparent when the above values of the thallium potentials are plotted against the logarithms of the ion concentrations, as in Fig. 1. The continuous straight line shows the way the potential would change with the ion concentration according to the Nernst equation; the points enclosed in circles show the values obtained by Neumann. These obviously neither follow the



Log. ion concentration.
Fig. 1.



Log. ion concentration.
Fig. 2.

---

[1] *Z. physik. Chem.*, 14, 193 (1894).

[2] N. E. stands for normal electrode. A positive electromotive force, E, indicates always that the current tends to pass in the cell from left to right.

theoretical curve nor show any great regularity in their deviation therefrom.

The dependence of the thallium potential upon the concentration of thallous ion has ben recently studied by Abegg and Spencer[1] with various concentrations of thallous nitrate, chloride, sulphate and hydroxide. Their results for the potentials in different concentrations of thallous chloride are reproduced in Fig. 2, where the continuous line again represents the theoretical change of potential with the concentration. The authors conclude that the Nernst formula is not even approximately true for the thallium electrode. This conclusion is also reached by Shukow [2]

In all cases studied the potential changes less rapidly with the concentration than theory requires, and in all cases the deviations are greater the more dilute the solutions. This could readily be explained by assuming that the thallium electrode is oxidized by the oxygen contained in the solution, thus increasing the concentration of thallous ion next the electrode. The percentage change of concentration thus produced would obviously be greater in the more dilute solutions. This possibility, however, was considered both by Zhukov and by Abegg and Spencer, and in both cases precautions were taken which seemed adequate to preclude it.

Any other explanation must depend upon the assumption of some abnormality in thallous ion. In fact Denham[3] has claimed that metallic thallium in the presence of thallous ion forms sub-thallous ion. Kohlrausch and von Steinwehr[4] have suggested that a somewhat anomalous trend in the conductivity of thallous chloride indicates the tendency on the part of thallium to form complex ions. Finally we might surmise the formation of a double ion Tl_2^{++} analogous to the one which is supposed to exist in the case of univalent mercury. On account of these various possibilities it seemed desirable to investigate the subject more closely from the experimental side.

The Effect of Thallous Ion Concentration upon the Potential of Thallium.

The solutions used in this investigation were made from salts carefully purified by suitable recrystallizations, and from doubly distilled water. The metallic thallium employed came from two independent sources (Kahlbaum, Eimer and Amend) and both varieties proved to be identical in electromotive behavior. In determining the effect of the various solutions upon the potential, the kind of thallium electrode used was unimportant provided that it be constant and reproducible. A concentrated but

[1] *Z. anorg. Chem.*, 46, 406 (1905).

[2] *Ber.*, 38, 2691 (1905).

[3] *Proc. Chem. Soc.*, 24, 76 (1908).

[4] *Ber. Berlin. Akad.*, 1902, 581.

unsaturated thallium amalgam, prepared with doubly distilled mercury, proved most satisfactory. The amalgam used contained 20 per cent. thallium and was kept in a pipette provided with stopcocks, where it was protected from atmospheric moisture and could be withdrawn as needed. All measurements were made in a thermostat maintained at 25.00°.

The solutions were prepared by dissolving known weights of the dried salts, or from saturated solutions obtained by shaking the salt and water together in the thermostat for 24 hours. These solutions were introduced into electrode vessels of the ordinary "half-cell" type together with the 20 per cent. amalgam. These half cells could then be measured against one another or against a single one chosen arbitrarily. The one so chosen contained a saturated thallous chloride solution with an excess of the solid salt lying above the amalgam.

The first series of experiments was made with solutions of thallous chloride and nitrate. On account of the almost equal mobility of thallous ion and chloride ion the liquid potential between different solutions of thallous chloride may be entirely neglected. Between electrodes in chloride and nitrate of the same concentration a small difference was observed corresponding as nearly as could be observed to the calculated potential[1] between the liquids. It was found possible to eliminate this difference by interposing a normal potassium chloride solution between the two liquids, and this was done in the succeeding experiments.

The results of this series are given in Table I where the first column shows the salt used and its concentration (*S* denotes a saturated solution). The third column gives the potential between the electrode in question and the one in saturated thallous chloride. Each value is the mean of several determinations, which, in the concentrated solutions, were very concordant.

TABLE I.

	Volt.		Volt.
$TlNO_3$ 1/10 *N*	−0.0414	TlCl 1/200 *N*	+0.0240
$TlNO_3$ 1/30 *N*	−0.0175	$TlNO_3$ 1/200 *N*	+0.0228
$TlNO_3$ 1/40 *N*	−0.0112	TlCl 1/5 *S*	+0.0301
TlCl *S*	0.0	TlCl 1/400 *N*	+0.0356
TlCl 1/100 *N*	+0.0104	$TlNO_3$ 1/400 *N*	+0.0339
TlCl 1/2 *S*	+0.0144		

These values are plotted in Fig. 3 against the concentrations of thallous ion, the latter values being obtained with the aid of degrees of dissociation calculated from Kohlrausch's conductivity data. The solubility of thallous chloride at 25° is taken as 0.0161 *N*. This is the value obtained in perfect agreement both by Noyes[2] and by Kohlrausch.[3]

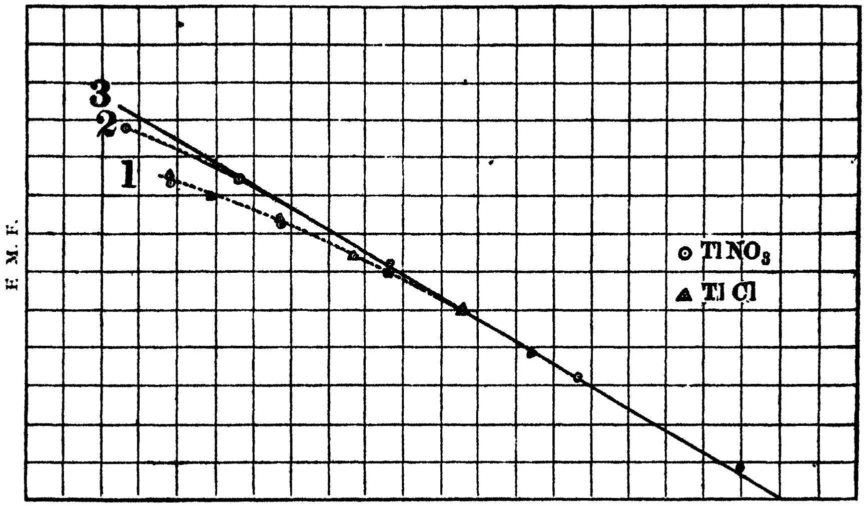
---

[1] See Lewis and Sargent, THIS JOURNAL, 31, 363 (1909).

[2] *Z. physik. Chem.*, 49, 296 (1904).

[3] *Ibid.*, 64, 149 (1908).

In the dilute solutions there is obviously an increasing divergence from the straight line (3) demanded by the Nernst equation. However, this divergence, although in the same direction, is so much smaller than that found by previous investigators, and the potentials measured were so much less certain in the dilute solutions than in the concentrated, that we were inclined to believe the apparently anomalous behavior of the dilute solutions to be due to some cause latent in the experimental method. This suspicion was confirmed when the solutions which had been used with the thallium electrodes were tested with phenolphthalein and found to be decidedly alkaline.



Log ion concentration

Fig. 3

This alkalinity must obviously be due to the oxidation of metallic thallium by dissolved oxygen. The small amount of thallous hydroxide thus produced is insufficient to produce an appreciable percentage increase in thallous ion concentration in the concentrated solutions, but evidently might be sufficient in the dilute solution to cause the low potentials observed. For this reason several dilute solutions were investigated further with two additional precautions. The first consisted in exhausting the solutions of air as far as possible,[1] the second in filling the electrode vessel first with solution and then introducing the amalgam through a capillary dipping below the surface of the solution. These changes resulted in an increase of 0.0008 volt in the potential of the electrode with saturated thallous chloride. The other new electrodes measured against this new thallous chloride electrode gave the values in Table II.

---

[1] It was found possible to exhaust a solution without appreciably changing its concentration, by boiling it for a minute or two under reduced pressure at a temperature of 25° to 30° C.

TABLE II.

	Volt.		Volt.
TlCl *S*	0	$TlNO_3$ 1/262 *N*	+0.0346
$TlNO_3$ 1/100 *N*	+0.0121	$TlNO_3$ 1/515 *N*	+0.0480

These data are shown also in Fig. 3, and are represented by the points lying on the second dotted curve (2). These points approach very close to the theoretical except at the highest dilution. Moreover, the solutions still gave a faint coloration with phenolphthalein, showing the presence of amounts of thallous hydroxide which, though very small, might affect the potential at high dilutions. Of the values thus far obtained those least likely to be affected by the oxidation of the electrode are undoubtedly those for the two most concentrated solutions, tenth- and thirtieth-normal $TlNO_3$, and the two most concentrated of the diluter solutions in which special precautions were taken, namely, saturated thallous chloride and hundredth-normal thallous nitrate. These values agree very closely with the Nernst formula and it seemed particularly desirable to obtain an equally reliable value for a more dilute solution, in order to test the formula over as wide a range as possible.

We had already observed that an electrode under saturated thallous chloride, with excess of solid thallous chloride, was more reproducible than one containing the same concentration of an unsaturated thallous salt. This was to be expected since a small amount of thallous ion accidentally added to saturated thallous chloride would be largely removed from the solution as solid thallous chloride. For this reason we decided to use for the most dilute solution a saturated solution of thallous bromide. This has a solubility at 25° of 0.00199 *N* according to the recent work of Kohlrausch,[1] whose measurements moreover agree perfectly with those of several other observers.

A saturated solution of this salt and an excess of the solid were placed in a specially designed electrode receptacle through which very pure hydrogen could be passed continuously, so as to bubble through the solution. When this process had been continued long enough to insure the removal of all the oxygen from the solution and the gas above it, by turning a stopcock the thallium amalgam was allowed to enter through a fine capillary. The electrode thus prepared gave, against the saturated TlCl electrode, a very constant potential of +0.0521 volt and the solution after long standing in contact with the electrode gave no coloration with phenolphthalein. We may therefore consider this potential as reliable as the four mentioned above. We reproduce these five values in Table III, which gives the concentration, *C*, of the salt used, the degree of dissociation, α, as obtained from conductivity measurements, the ion concentration, *C'*, the potential, *E*, against the saturated thallous chloride electrode, and the values of *E* calculated from the Nernst equation. These data are also plotted in Fig. 4.

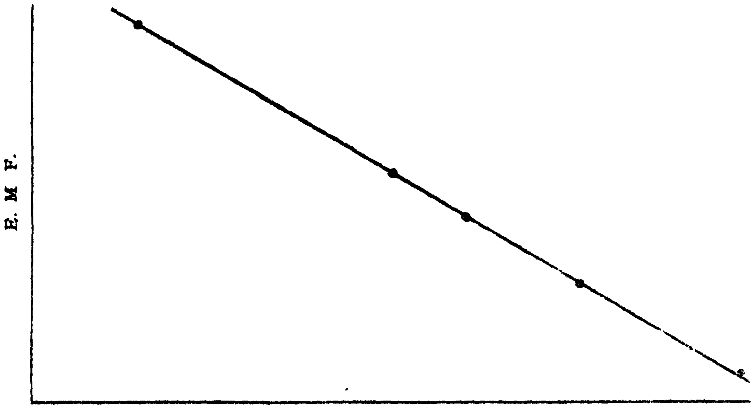
---

[1] *Z. physik. Chem.*, 64, 149 (1908).

TABLE III.

	C	α.	*C'*.	*E*.	*E* (calc.).
$TlNO_3$	0.100	0.79	0.0790	—0.0422	—0.0438
$TlNO_3$	0.0333	0.88	0.0293	—0 0183	—0.0182
$TlCl(S)$	0.0161	0.89	0.0143	0	(standard)
$TlNO_3$	0.0100	0.93	0.00930	+0.0113	+0.0113
$TlBr(S)$	0.00199	0.97	0.00193	+0.0513	+0.0516

The deviation of one and a half millivolts between the observed and calculated values for tenth-normal thallous nitrate is undoubtedly real, and not to be attributed to experimental error. Moreover such a real deviation from the Nernst equation in the direction found is to be expected in the case of a solution as concentrated as tenth-normal. There is much experimental evidence to show that if conductivity is taken as a measure of ion concentration, the ions (although much less abnormal in behavior than the undissociated substance) do not quite obey the laws of a perfect solution. The ratio of their activity[1] to their concentration, which should be constant, diminishes somewhat at the higher concentrations.[2]



Log. ion concentration.
Fig. 4.

The remaining values agree remarkably with the Nernst equation, the deviations being irregular, and amounting in no case to more than 0.0003 volt. This agreement, and the constancy of the potential when the solutions in the electrode vessels are stirred, we regard as strong evidence against the existence of the subthallous ion assumed by Denham.[3]

Instead then of finding any anomaly in the electromotive behavior of thallous ion, we may assert that the Nernst equation holds for the thallium electrode over a large range of concentration with greater accuracy than it has as yet been shown to do in the case of any other electrode.

---

[1] See Lewis, *Proc. Am. Acad.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907).

[2] In an article about to appear in THIS JOURNAL, Bray and Mackay point out an interesting case in which this rule is confirmed.

[3] *Loc. cit.*

The Thallium Electrode Potential.

In order to determine the absolute electrode potential of thallium, we must use an electrode of pure metallic thallium or some electrode that is its equivalent. It was shown by Kurnakov and Puschkin[1] that thallium and mercury form no solid compound above 15°. Sucheni[2] showed that mercury does not dissolve to any extent in solid thallium, and that a saturated solution of thallium in mercury therefore has the same potential as pure thallium. This fact, which we have also corroborated, enables us to use a paste of thallium and thallium amalgam in place of solid thallium, which like all solid metals gives an inconstant potential owing to uncontrollable surface variations.

A mixture of 55 parts thallium and 45 parts mercury was warmed until liquid in the electrode vessels. After cooling, the electrodes were rinsed with the solution to be used and the vessels then filled. After this rinsing, electrodes prepared without special precautions gave the same results as those prepared in the total absence of oxygen. The first experiments, with three electrodes of this type (in two of which the amalgams were made from samples of thallium of different origin) were made with saturated solutions of thallous chloride containing an excess of the solid chloride. In the first case no special precautions were taken, in the second the solution was freed from air by exhaustion, in the third by a stream of hydrogen. Against the normal electrode the electromotive forces were 0.7258, 0.7256, 0.7257, respectively. We may write, therefore,

$$\text{Tl, TlCl (sat.) N. E.; } E = 0.7257 \text{ volt.}$$

The ion concentration of thallium in the saturated chloride solution is 0.0143 N. From the Nernst equation,

$$\text{Tl, Tl}^+(N)\text{, Tl}^+(0.0143\ N)\text{, Tl; } E = 0.1087 \text{ volt.}$$

Adding these equations gives

$$\text{Tl, Tl}^+(N)\text{, N. E.; } E = \underline{0.6170 \text{ volt.}}$$

On account of the almost equal mobility of thallous and potassium ions, the liquid potential is here negligible. Therefore, the potential of the thallium electrode, when the normal electrode is taken as zero, is 0.6170 volt at 25°.[3]

We also investigated electrodes of saturated thallium amalgam under tenth-normal and normal potassium chloride saturated with thallous chloride. Electrodes of this type were used successfully by Sucheni and we find them, as was to be expected, much less affected by any oxidation of the electrode than the other types that have been used. The electrodes with tenth-normal potassium chloride gave against the normal electrode the following potentials in four experiments, the last one being made with a new potassium chloride solution prepared from salt of a different origin. (1) 0.7707, (2) 0.7704, (3) 0.7705, (4) 0.7708. The average is therefore,

---

[1] *Z. anorg. Chem.*, 30, 86 (1902).

[2] *Z. Elektrochemie*, 12, 726 (1906).

[3] As in other cases, this is not the potential against a real normal solution of thallous ion, but against a sort of hypothetical normal solution, between which and a dilute solution the Nernst formula would hold. This potential would in any case be more useful in calculation than that against the real normal solution, even if the latter value could be obtained.

$$\text{Tl, TlCl (solid), KCl } (1/10\,N),\text{ N. E.; } E = 0.7706 \text{ volt.}$$

From this value also it is possible to calculate the normal potential of thallium, although this calculation is less justifiable than the one above, since it assumes the validity of the laws of the perfect solution up to a higher concentration. The solubility product of TlCl is (0.0143),[2] and the concentration of Cl^- due to the potassium chloride may be taken as 0.085, allowing for the degree of dissociation, in the presence of thallous chloride; then, if x is the concentration of thallous ion, we obtain from the solubility-product rule,

$$(0.085 + x)\,x = (0.0143)^2.$$

Hence $x = 0.00234$ and the above equation for electromotive force may be written

$$\text{Tl, Tl}^+ (0.00234\,N),\text{ N. E.; } E = 0.7706 \text{ volt.}$$

From the Nernst formula,

$$\text{Tl, Tl}^+ (N),\text{ Tl}^+ (0.00234\,N),\text{ Tl; } E = -0.1555 \text{ volt.}$$

Hence,

$$\text{Tl, Tl}^+(N),\text{ N. E.; } E = 0.6151 \text{ volt.}$$

The difference of nearly two millivolts between this value and the one obtained above is not to be ascribed to experimental error, but was to have been predicted from the principle stated above, namely that when we calculate concentrations in the ordinary way the activity of an ion in tenth-normal solution is always lower than that calculated from the behavior of more dilute solutions. The chloride ion from the tenth-normal potassium chloride has really then a smaller effect on the solubility of thallous chloride than we have ascribed to it when we assumed the complete validity of the ideal laws upon which the solubility-product rule is based. We shall adhere therefore to the first value, 0.6170 v., as the potential of the thallium electrode.

We also investigated saturated thallium amalgam in normal potassium chloride saturated with thallous chloride, and this furnished the most constant electrode of all those that we measured. With reasonable care it should give fully as reproducible a potential as the normal calomel electrode. Against the latter it has the following potential:[1]

$$\text{Tl, TlCl (solid), KCl } N,\text{ N. E.; } E = 0.8227 \text{ volt.}$$

---

[1] It is worth noting that the difference of 0.0521 v. between the electrodes in N and $1/10\,N$ KCl is almost identical with the difference of about 0.0526 v. between the normal and tenth-normal calomel electrodes.

This electrode, although it gives entirely reproducible potentials, shows a gradual increase of potential on long standing. This phenomenon had been observed to a greater degree with the other electrodes. Electrodes in saturated solutions of thallous chloride in water, 1/10 *N* KCl and *N* KCl respectively, increased in potential after four months' standing by 0.0038 volt, 0.0014 volt, and 0.0004 volt. We have not ascertained the cause of this increase. It is not due to any change in the amalgam, since in every case the original potential is obtained when the electrode vessel is refilled with a fresh solution.

Summary.

Contrary to some views previously published, there is nothing anomalous in the electromotive behavior of thallous ion, nor do we find any evidence of the existence of a sub-thallous ion.

Previous measurements of the thallium potential have been vitiated by the oxidation of the electrode and the consequent increase in thallous ion concentration. When such oxidation is avoided the Nernst formula is obeyed more closely than has been shown to be the case with any other electrode.

The assumption of the validity of the Nernst formula and the solubility-product rule (ion concentration being measured by conductivity) leads to measurable errors when the concentration is as high as tenth-normal, and the direction of these errors can be predicted.

The potential of pure thallium in saturated solutions of thallous chloride in water, in 1/10 *N* KCl and in *N* KCl were measured. The potential of pure thallium against (hypothetical) normal thallous ion is 0.6170 volt at 25° when the normal calomel electrode is taken as zero.

This work was completed in the summer of 1908.

Note.—Since this paper was written our attention has been called to an article by Brislee[1] who has investigated thallium potentials with precautions against the oxidation of the electrodes. He also finds no striking deviation from the Nernst equation although the variations which he observes are much larger than ours. This is doubtless because electrodes of solid thallium were used and because the work was not done in a thermostat. His value for the thallium electrode potential differs considerably from ours. We give below a table of values for the e. m. f. of Tl, Tl^+N, N. E. calculated from the results of the various observers whose work has been mentioned above. All the values are based on experiments with saturated thallous chloride.

	E. M. F.
Neumann	0.605
Abegg and Spencer	0.614
Brislee	0.602
Lewis and von Ende	0.6170

---

[1] *Trans. Faraday Soc.*, 4, 157 (1909).

Our value, obtained at 25°, we regard as undoubtedly accurate within a few tenths of a millivolt: Brislee's value was obtained in the neighborhood of 17° and the wide difference between the two values may be in part due to the difference in temperature, which would indicate, however, an exceptionally large temperature coefficient for the thallium electrode.

BOSTON, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 48.]

THE IONIZATION OF SALTS IN MIXTURES WITH NO COMMON ION.

BY MILES S. SHERRILL.

Received April 14, 1910.

Contents.

1. Purpose of the Investigation. 2. Principles Relating to the Ionization of Salts in Mixtures. 3. The Experimental Method. 4. The Conductance Data. 5. Method of Calculation and Results. 6. Discussion of the Results.

1. Purpose of the Investigation.—The general purpose of this investigation was to determine what modification must be made of the empirical principles which have been found to express the ionization of salts in mixtures with a common ion, in order that they may be applicable also to mixtures with no common ion; in other words, to determine the *general* law governing the ionization relations of salts.

Although many researches have been carried out on the conductance of mixtures with a common ion, few data exist upon mixtures with no common ion suitable for the purpose just mentioned.[1] At the suggestion of Professor A. A. Noyes, this investigation was therefore undertaken, the plan being to measure the conductance of mixtures of two salts with no common ion, and to compare the results with the conductance calculated by the principle discussed in the following section. The salts chosen were potassium chloride and sodium sulphate, and sodium chloride and potassium sulphate. Thus mixtures of salts of two ionic types could be prepared, whereby a more satisfactory test of the theory would be afforded.

2. Principles Relating to the Ionization of Salts in Mixtures.—The principles already established may be first briefly reviewed.

The mass-action law requires that the ionization γ of any salt vary with the concentration C, in accordance with the equation:

$$\frac{(\gamma C)^n}{(1-\gamma)C} = K. \qquad (1)$$

where K is the ionization constant for the salt, and n is the number of ions produced by the ionization of 1 molecule of the salt. The numerical value for n should therefore vary with the ionic type of salt, being 2 for uni-univalent salts, like potassium chloride, 3 for uni-bivalent salts like potassium sulphate, etc. As is well known, however, the mass-action law does not apply, even approximately, to the ionization of salts, strong acids, and bases when the conductance ratio Λ/Λ_0 is taken as a measure of the ionization.[1]

---

[1] The only measurements that exist seem to be those of Barmwater (*Z. physik. Chem.*, 28, 427 (1899)), on certain mixtures of uni-univalent salts.

Kohlrausch,[2] Rudolphi,[3] and van't Hoff[4] first proposed various empirical functions containing only a single constant for the purpose of expressing the change of ionization with the dilution. Storch[5] then suggested that, in order to secure closer agreement with the observed values, a general expression of the form of equation (1) be employed, the exponent n being regarded as a second empirical constant to be derived for each particular salt from the conductance measurements. van't Hoff[6] had already shown that an approximate agreement between the formula and the existing data could be secured in the case of a large number of di-ionic salts by taking $n = 1.5$. Storch showed that a nearly complete agreement in the case of the eight di-ionic and four tri-ionic substances studied was attained up to 0.1 normal by assuming values of n varying only within the limits 1.42 and 1.52. Bancroft[7] showed that Storch's formula with values of n varying within about the same limits was applicable to certain other di-ionic salts. By the extended investigations made in this laboratory it has been shown that the same is true also for tri-ionic and tetra ionic salts, and for the salts of all three types through a very wide range of temperature Thus the values of n obtained, though varying somewhat with the nature of the salt and the temperature, all fall within the narrow limits of 1.40 to 1.55.[8]

Equation (1) may also be written in the following form, which expresses the ionization as a function of the ion concentration ($C\gamma$):

$$\frac{\gamma}{1-\gamma} = K(C\gamma)^{1-n}. \qquad (2)$$

A study of the conductance of mixtures of two salts with a common ion has thrown further light on the ionization relations of salts. The results of such measurements can be satisfactorily expressed by the following principle derived from theory of isohydric solutions of Arrhenius,[9] and shown, most fully by the investigations of MacGregor, McIntosh, Archibald, and McKay,[1] to be valid not only for uni-univalent salts, but also for those of higher types, even in cases, as has been pointed out by Noyes,[2] where the mass-action law would require a very different effect. In a mixture of two salts with a common ion each salt has a degree of ionization equal to that which it has when alone present in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture.

---

[1] For general discussion of this subject see Noyes, *Z. physik. Chem.*, **52**, 635 (1905); *Science*, **20**, 584 (1904).

[2] *Wied. Ann.*, **26**, 200 (1885); **50**, 394 (1893).

[3] *Z. physik. Chem.*, **17**, 385 (1895).

[4] *Ibid.*, **18**, 300 (1895).

[5] *Ibid.*, **19**, 13 (1896).

[6] *Loc. cit.*

[7] *Ibid.*, **31**, 188 (1899).

[8] THIS JOURNAL, **30**, 343 (1908); **31**, 1000 (1909).

[9] *Z. physik. Chem.*, **2**, 285 (1888); **31**, 218 (1899).

This principle evidently shows that the ionization of any salt is the same function of the ion concentration, whether the salt is present alone or together with another salt with a common ion. Therefore, in correspondence with equation (2), it may be expressed as follows:

$$\frac{\gamma_1}{1-\gamma_1} = K_1(C_1\gamma_1+C_2\gamma_2)^{1-n_1}; \text{ and } \frac{\gamma_2}{1-\gamma_2} = K_2(C_1\gamma_1+C_2\gamma_2)^{1-n_2}; \qquad (3)$$

the subscripts referring to the two salts, respectively. These equations may readily be transformed into the following ones:

$$\frac{C_1\gamma_1(C_1\gamma_1+C_2\gamma_2)}{C_1(1-\gamma_1)} = K_1(C_1\gamma_1+C_2\gamma_2)^{2-n_1}; \text{ and}$$

$$\frac{C_2\gamma_2(C_1\gamma_1+C_2\gamma_2)}{C_2(1-\gamma_2)} = K_2(C_1\gamma_1+C_2\gamma_2)^{2-n_2}. \qquad (4)$$

That signifies that in a mixture of salts with a common ion the ratio of the product of the concentrations of the constituent ions of each salt to the concentration of its un-ionized part is proportional to the equivalent concentration of the common ion raised to the (2-n) power. In this case of a mixture of salts with a common ion, it is to be noted that the expression (γ_1C_1 + γ_2C_2) for the concentration of the common ion is also the expression for the sum of the equivalent concentrations (Σi) of all the positive or negative ions. If, as seems reasonable, it is this "total ion concentration" which in general determines the equilibrium, then for any salt of the general type A_xB_y present in any solution where the total equivalent ion concentration is (Σi), the following expression will hold true:

$$\frac{(A)(B)}{(A_xB_y)} = K(\Sigma\text{i})^{2-n}. \qquad (5)$$

It is evident from this equation that for a given total ion concentration in the solution the ratio (A)(B)/(A_xB_y) has a definite value which can be calculated from the values of K and n that may be derived by equation (1) from the ionization values of the salt when present in water alone. This makes it possible to calculate the concentrations of all the ions and the un-ionized substances present in a solution containing any definite mixture of salts, as will be shown later.

---

[1] *Trans. N. S. Inst. Sci.*, Vols. 9 and 10 (1895–1899).

[2] *Loc. cit.*

3. The Experimental Method.—Exactly 0.2 normal solutions of the four separate salts[1] were made by weighing out the ignited substances, transferring them to a two-liter graduated flask, and adding sufficient conductivity water to bring the solution at 18° to the graduation mark. The more dilute salt solutions and the solutions of the mixed salts were prepared by mixing with the aid of carefully calibrated pipettes definite volumes of the stock solutions with water or with each other. The specific conductance of the water used did not exceed 0.9×10^{-6} reciprocal ohms.

The conductance measurements were made at 18°, observing the usual precautions, in a U-tube of one of the forms described by Kohlrausch and Holborn,[2] with platinized electrodes. The conductance capacity of this cell was calculated from the conductance values given by Kohlrausch and Maltby[3] for various solutions of potassium chloride. The thermometer, slide-wire, and resistance coils used had all been calibrated.

4. The Conductance Data.—The results of the measurements with the separate salts are given in Table I.

TABLE I.

	Specific conductance × 1000 at 18°.			
Equiv. conc.	NaCl.	KCl.	Na_2SO_4.	K_2SO_4.
0.2	17.546	21.592	13.99	17.57
0.1	9.202	11.203	7.707	9.491
0.05	4.785	5.787	4.182	5.098

The specific conductance values for potassium chloride, sodium chloride, and potassium sulphate agree within 0.1 per cent. with the latest measurements of Kohlrausch and Maltby and Kohlrausch and Grüneisen.[1] Compared with the earlier conductance values of Kohlrausch, marked deviations, amounting in the stronger solutions to 2 per cent., exist in the case of sodium sulphate.

In Table II are given the results obtained with the mixtures. The first column gives the number of the mixture. The next four columns show the equivalent concentrations of the solutions from which each mixture was prepared. The next four columns show the relative volumes of these solutions which were mixed. The last column gives the specific conductance (×1000) in reciprocal ohms of the mixture at 18°.

It may be pointed out that a check upon the purity of the salts and the preparation of the solutions is afforded by the complete agreement of the conductances of mixtures Nos. 3 and 7, of which the former was prepared from sodium chloride and potassium sulphate and the latter from potassium chloride and sodium sulphate.

[1] These salts were kindly furnished to me by Mr. A. C. Melcher, who had prepared them in a pure state for other conductivity work.

[2] *Leitvermögen der Elektrolyte*, Fig. 10, p. 16 (1898).

[3] See *Landolt-Börnstein-Meyerhoffer Tabellen*, 3 *Auflage*, p. 744.

TABLE II.

Mixt. No.	Equivalent concentration.				Relative volumes mixed.				Specific cond. × 1000.
	NaCl.	K_2SO_4	KCl.	Na_2SO_4.	NaCl.	K_2SO_4.	KCl.	Na_2SO_4.	
1	0.2	0.2	...	...	4	1	.	.	17.52
2	0.2	0.2	...	...	2	1	.	.	17.53
3	0.2	0.2	...	...	1	1	.	.	17.52
4	0.2	0.2	...	...	1	2	.		17.52
5	0.2	0.2	...	...	1	4	.	.	17.52
6	...	...	0.2	0.2	.	.	1	2	16.29
7	...	...	0.2	0.2	.		1	1	17.52
8	...	...	0.2	0.2	.	.	2	1	18.81
9	0.1	0.1	...	...	4	1	.	.	9.262
10	0.1	0.1	...	...	2	1	.	.	9.303
11	0.1	0.1	...	...	1	1	.	.	9.346
12	0.1	0.1	...	..	1	2	.	.	9.378
13	0.1	0.1	...	.	1	4	.	.	9.430
14	...	...	0.1	0.1	.	.	2	1	9.933
15	...	...	0.1	0.1	.	.	1	2	9.778

5. *Method of Calculation and Results.*—When two salts with no common ion (for example NaCl and K_2SO_4) are mixed there are formed by metathesis two other salts (KCl and K_2SO_4). In any definite mixture of this kind the composition shows the value of the total sodium (ΣNa), total potassium (ΣK), total sulphate (ΣSO_4), and total chloride (ΣCl). The various forms in which these constituents exist are expressed by the following equation, in which the symbols within parentheses represent the *equivalent* concentrations:

$$(\Sigma \text{Na}) = (\text{Na}^+) + (\text{NaCl}) + (\text{Na}_2\text{SO}_4). \qquad (6)$$

$$(\Sigma \text{K}) = (\text{K}^+) + (\text{KCl}) + (\text{K}_2\text{SO}_4). \qquad (7)$$

$$(\Sigma \text{SO}_4) = (\text{SO}_4^{=}) + (\text{K}_2\text{SO}_4) + (\text{Na}_2\text{SO}_4). \qquad (8)$$

$$(\Sigma \text{Cl}) = (\text{Cl}^-) + (\text{NaCl}) + (\text{KCl}). \qquad (9)$$

According to the principle stated in the second section, the ratio of the product of the concentrations of the ions of any one salt to that of its un-ionized part is proportional to the total equivalent ion concentration raised to the (2-*n*)-power. (This ratio will, in the following discussion, be designated the ion-product-ratio of the salt.)

This principle applied to each salt in the mixture furnishes the four additional equations that are needed in order to make it possible to solve for the concentration of each of the eight substances present. The equations are:

$$\frac{(\text{Na}^+)(\text{Cl}^-)}{(\text{NaCl})} = K_1(\Sigma i)^{2-n_1}. \qquad (10)$$

$$\frac{(\text{K}^+)(\text{Cl}^-)}{(\text{KCl})} = K_2(\Sigma i)^{2-n_2}. \qquad (11)$$

$$\frac{(\text{Na}^+)(\text{SO}_4^{=})}{(\text{Na}_2\text{SO}_4)} = K_3(\Sigma i)^{2-n_3}. \qquad (12)$$

$$\frac{(K^+)(SO_4^=)}{(K_2SO_4)} = K_4(\Sigma i)^{2-n_4}. \qquad (13)$$

In these equations, $(\Sigma i) = (Na^+) + (K^+)$ or $(Cl^-) + (SO_4^=)$, and K_1, K_2, K_3, K_4, and n_1, n_2, n_3, n_4 are the coefficients and exponents for the respective salts which occur in the dilution formula, $(\gamma C)^n = KC(1-\gamma)$ expressing their ionization when present in water alone.

The above equations were easily solved by trial in the following way: The separate ion concentrations were estimated, and the numerical value of the ion-product-ratio for each salt corresponding to the sum of these ion concentrations was determined. This value for the salt in question was obtained from a curve plotted with its ion-product-ratios as abscissas and the corresponding ion concentrations as ordinates, the data given in Table I for the salts in water alone being employed. From these values of the ion-product-ratios and the values of the ion-concentrations estimated at the start, the concentrations of the un-ionized parts of the salts were calculated by equations (10) to (13). By substitution of the latter concentrations in equations (6) to (9) were obtained better values for the separate ion-concentrations. With these new values of the ion-concentrations the whole process was repeated until all eight equations were satisfied.

The specific conductance L of any given solution was then calculated from the equivalent concentrations, obtained as just described, and from the equivalent conductances (Λ_K, etc.), at zero concentrations of the separate ions by the equation

$$1000\,L = (Na^+)\Lambda_{Na} + (K^+)\Lambda_K + (SO_4^=)\Lambda_{SO_4} + (Cl^-)\Lambda_{Cl}. \qquad (14)$$

The values used for the equivalent conductances of the ions were those given by Kohlrausch,[1] namely, $\Lambda_{Na} = 43.6$, $\Lambda_K = 64.7$, $\Lambda_{SO_4} = 68.4$, and $\Lambda_{Cl} = 65.4$.

The results of the calculations are given in Table III. That the values given actually satisfy equations (6) to (9) can be readily proved by direct summation; and that they satisfy equations (10) to (13) can be shown by calculating the ion-product ratios and comparing these with those plotted for the salts in water alone, as above described.

6. *Discussion of the Results.*—A consideration of the last column of percentage differences shows that in the case of the first eight mixtures, in which the total salt concentration was 0.2 normal, the calculated conductance is greater by an average amount of 0.48 per cent., and that the variations from this average in the case of the mixtures with different proportions of sulphate and chloride are insignificant. In the case of the last seven mixtures, in which the total salt concentration was 0.1 normal, the same is true except that the average value of the percentage

---

[1] *Landolt-Börnstein-Meyerhoffer Tabellen*, p. 763.

difference is about one-half as large, namely 0.27 per cent., indicating that the deviation would probably be scarcely appreciable at 0.05 normal.

TABLE III.

Mixture	Concentrations in milli-equivalents per liter.								Spec cond × 1000.		
No.	NaCl.	KCl.	Na_2SO_4.	K_2SO_4.	Na^+.	K^+.	Cl^-.	$SO_4^=$.	Calc	Obs.	% Diff.
1	24.55	5.35	12.85	2 75	122.60	31 90	130 00	24 40	17 59	17.52	0.40
2	16 86	7 40	17.75	7.65	98 69	51 62	109 10	41.27	17 60	17 53	0 45
3	9.33	8 24	19.77	17 23	70.90	74 53	82 43	63.00	17 61	17 52	0.51
4	4.07	7 24	17.43	30.59	45 17	95.50	55 36	85 31	17 61	17.52	0 51
5	1 44	5 17	12 38	43 71	26 18	111.10	33.39	103 90	17.62	17.52	0.57
6	8 16	3 64	34.54	15 15	90 60	47 88	54.87	83 61	16 36	16.29	0 43
7	9 32	8.25	19 77	17 23	70 91	74.52	82 43	63 00	17.61	17.52	0.51
8	8.45	14.80	9 01	15.50	49 21	103 00	110 10	42.16	18 89	18 81	0.48
9	9.82	2.20	5.29	1.18	64 89	16 62	67 98	13.53	9 276	9 262	0 15
10	6 75	3 02	7.31	3 26	52 61	27 05	56.90	22 76	9 321	9 303	0 19
11	3.75	3 37	8.13	7 31	38 12	39.32	42 88	34 56	9.374	9 346	0 30
12	1 64	2 97	7 16	12 92	24.53	50 78	28 72	46 59	9 420	9.378	0 45
13	0.58	2.11	5 08	18 50	14 34	59 39	17 31	56 42	9 460	9 430	0.32
14	3 37	6 04	3 68	6 57	26 28	54.06	57 26	23.08	9 964	9 933	0 31
15	3 29	1 49	14 27	6 45	49 11	25 39	28 55	45.95	8 795	8 778	0 19

Since the conductance is substantially determined by the sum of the concentrations of the ions (irrespective of their separate concentrations), these results show that *when the concentrations of the separate ions of the salts in the mixtures are calculated by the principle expressed by the equation* $(A)(B)/(A_xB_y) = K(\Sigma i)^{2-n}$ *the sum of the ion concentrations is obtained with an accuracy of about* $^1/_2$ *per cent. at 0.2 normal and of about* $^1/_4$ *per cent. at 0.1 normal.*

The possibility must, of course, be recognized that a compensation takes place owing to the un-ionized tri-ionic salts being present in a larger or smaller proportion and the un-ionized di-ionic salts being present in a correspondingly smaller or larger proportion than that calculated. This might be the case, for example, if the ionization relations of the di-ionic and tri-ionic salts were determined by a different principle, instead of by the same principle, as has been assumed. All that can be said is that there are at present no facts known that make necessary this more complicated assumption.

One possibility deserves, however, brief consideration because of its possible theoretical significance. It might be assumed, namely, that the law of the equilibrium for a tri-ionic salt like K_2SO_4 should be written, in closer correspondence with the mass-action law, in the form

$$\frac{(K^+)^2(SO_4^=)}{(K_2SO_4)} = K(\Sigma i)^{3-n}, \text{ instead of } \frac{(K^+)(SO_4^=)}{(K_2SO_4)} = K(\Sigma i)^{2-n}.$$

When the salt is present in water alone or in a mixture with another potassium salt, these two expressions are identical, since then $(\Sigma i) =$

(K^+); but this is not true in any case where other positive ions are present, for example in mixtures with another sulphate, or in mixtures with no common ion like those above considered. Making the assumption that equations of the first form hold for potassium and sodium sulphates (in place of equations (12) and (13)) and that the other equations (6) to (11) hold true as before, the composition and conductance of Mixture No. 3 was calculated with the following result:

Concentrations in milli-equivalents per liter.								Spec cond. × 1000.		
NaCl.	KCl.	Na_2SO_4.	K_2SO_4.	Na^+.	K^+.	Cl^-.	$SO_4^{=}$.	Calc.	Obs.	% Diff.
9.70	8.40	12.40	10.91	77.9	80.7	81.9	76.7	19.22	17.52	9.6

It is seen that the conductance calculated under this assumption deviates very greatly (9.6 per cent. from the observed value).

BOSTON, April 10, 1910.

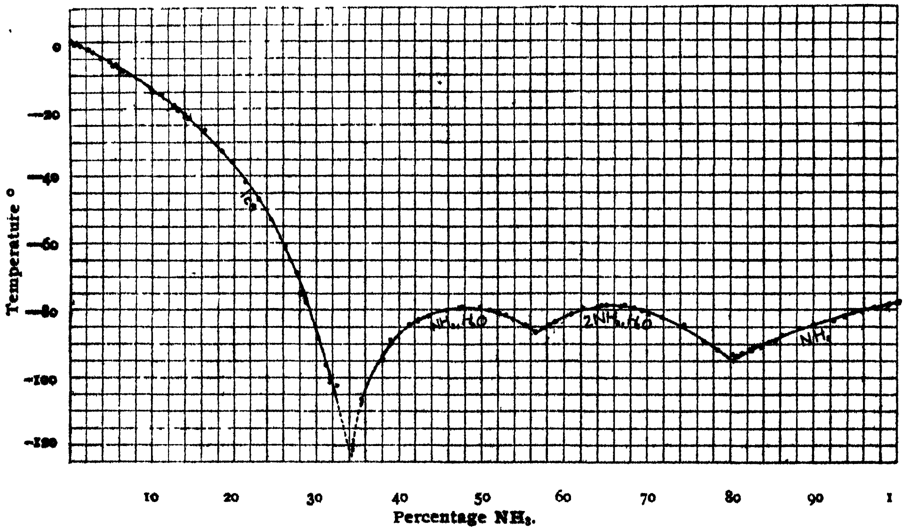
THE SOLID HYDRATES OF AMMONIA. II.

BY FRANK F. RUPERT.

Received April 11, 1910.

In a previous paper[1] the author gave the freezing-point curve for the system ammonia-water, showing the existence of two hydrates. Since then the work has been repeated, making a larger number of freezing-point determinations, and using better aids to accuracy.

The method used was substantially that described in the previous paper. Corrections were made for the weight of the ice inevitably collecting on the tube containing the solution, while being inserted in the vacuum tube. This amounted to 0.05 gram, with a possible error of 0.02 gram, in a total of 10 to 20 grams.



---

[1] THIS JOURNAL, 31, 866 (1909).

Temperatures above —100° were determined by using a standardized toluene thermometer, and are probably correct to within 0.5°; below that temperature by a thermo-couple standardized by comparison with the thermometer and with liquid air, but on account of the high viscosity of the solution, and consequent supercooling, the results for the latter determinations are unsatisfactory.

The table of freezing points follows:

Per cent NH_3.	Freezing point.	Per cent. NH_3.	Freezing point.	Per cent NH_3	Freezing point.
0.6	—0.6	30.2	—87.9	65.1	—79.0
0.7	—0.5	31.1	—96.0	66.9	—79.1
1.2	—1.0	31.7	Below —100.1	67.4	—78.6
2.1	—2.2	32.9	—102.5	68.4	—79.4
2.2	—2.2	34.5	Below —120.0	69.3	—80.2
2.9	—3.7	35.5	Below —101.5	70.1	—81.0
3.8	—5.0	38.0	—94.5	71.9	—82.0
4.0	—4.6	39.0	—88.8	74.3	—84.6
4.9	—5.9	41.4	—84.5	76.9	—88.8
5.1	—7.1	42.4	—84.2	78.6	—92.0
5.5	—7.0	42.4	—83.9	80.3	—92.9
5.7	—7.3	43.7	—82.0	80.8	—93.4
6.5	—8.5	45.9	—80.0	81.3	—92.8
6.7	—8.5	47.1	—79.6	82.3	—91.9
9.9	—13.4	47.7	—79.3	82.5	—92.4
11.1	—15.5	49.8	—79.3	82.8	—90.4
12.6	—19.0	51.1	—80.0	83.7	—90.6
13.2	—20.2	52.0	—80.6	84.9	—89.6
14.7	—22.9	52.2	—81.0	85.2	—88.8
16.4	—26.8	53.1	—81.8	86.1	—87.1
18.3	—32.6	53.9	—82.8	88.2	—85.3
19.6	—35.3	55.3	—84.2	90.0	—84.2
21.4	—41.9	56.7	—86.2	92.4	—82.9
23.0	—46.8	58.1	—84.9	93.6	—81.7
24.5	—52.6	58.9	—83.6	94.8	—81.0
26.1	—60.7	60.9	—81.2	95.7	—80.3
27.6	—68.5	62.2	—79.5	97.4	—79.4
28.5	—75.0	64.0	—79.4	98.9	—78.6
28.7	—77.8	64.6	—79.0	100.0	—78.0

The accompanying curve clearly shows two maxima, which do not differ from the theoretical compositions of NH_4OH and $(NH_4)_2O$, 48.6 and 65.4 per cent. ammonia respectively, by more than the experimental error. The eutectic points are: H_2O — NH_4OH, not determined; NH_4OH — $(NH_4)_2O$, —87°, 56.5 per cent. NH_3; $(NH_4)_2O$ — NH_3, —94°, 80.3 per cent. NH_3. Both ammonium hydroxide and ammonium oxide form fine white crystalline masses.

This work confirms the conclusion of the previous paper, namely, that ammonia forms two, and only two solid hydrates.

UNIVERSITY OF KANSAS.

THE INFLUENCE OF THE MAGNETIC FIELD ON THE PASSIVE STATE OF IRON.

By Horace G. Byers and Marc Darrin.

Received April 11, 1910.

In an article[1] by one of us it was shown that the passive state of iron may be produced in an anode in numerous electrolytes by a definite current density, and reference was made to the work of Fredenhagen[2] showing the same fact though incorrectly ascribed to the electromotive force employed. In an article by Nichols and Franklin[3] it was shown that the passive state of iron in nitric acid may be destroyed by placing the iron in a magnetic field of great intensity. It seemed of interest, therefore, to determine whether the passive state of iron as an anode might likewise be influenced by the magnetic field. To determine this question a number of experiments were carried out, but it was found impossible to destroy the passive state, when once established, by any magnetic field which we were able to produce with the apparatus available. Nevertheless, a distinct influence of the magnetic field upon the transition from the active

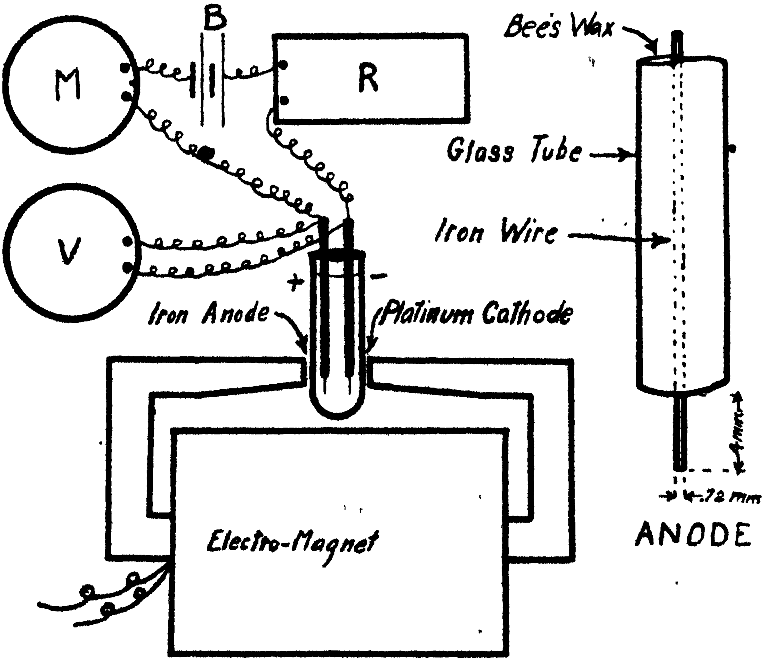


Fig. 1.

APR 1910 MARC DARRIN

---

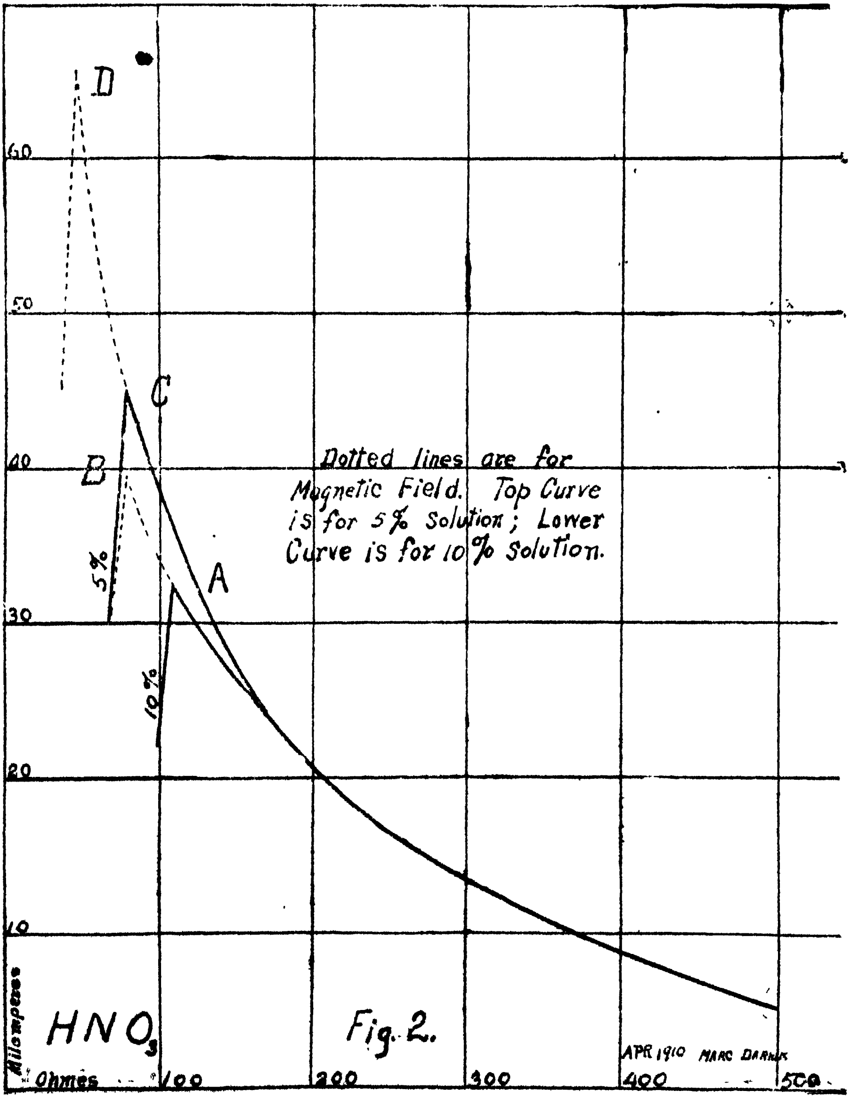
[1] This Journal, 30, 1718 (1908).

[2] *Z. physik. Chem.*, 63, 1 (1908).

[3] *Am. J. Sci.*, [3] 31, 272 (1886); [3] 34, 419 (1887).

to the passive state was demonstrated in several solutions, the details of the work being given below. It should be noted that not only is the transition from the active to the passive state of iron when used as an anode produced by a given current density, but that this transition point is extremely sharp and well defined.

Experimental Method.—The apparatus was connected as shown in Fig. 1. A 20 cc. test tube, containing the electrolyte, was placed between the poles of a powerful electromagnet (5825 turns of No. 18 wire; run by 110 volts



Dotted lines are for Magnetic Field. Top Curve is for 5% Solution; Lower Curve is for 10% Solution.

Fig. 2.

d. c.; amperage, 3 amp.; distance between poles 2 cm.; area of poles 7 sq. cm.; diameter of coil 16 cm.; length of coil 17 cm.). The anode was made by sealing into a glass tube, with beeswax, a piece of soft piano wire (diameter 0.72 mm.) such that only 4 mm. was exposed at the immersed end; the cathode consisted of a small strip of platinum foil at the end of a similar glass rod. The electrodes were put in series with two U. S. storage cells *B* (giving a constant current of about 5 v.), a rheostat *R* and a delicate Weston milliammeter *M* reading directly to half milliamperes. A voltmeter *V*, with a telegraph key, was connected across the circuit between the two electrodes. When the iron anode was active, the voltmeter would indicate but slight differences in potential between the two electrodes, and the milliammeter would show between 10 and 70 milliamperes passing through the circuit; when the iron changed to the passive state, there was a sharp rise in the voltmeter (to about 4 v.) and a corresponding drop in the milliammeter of about 10 milliamperes.

Experimental Results: Nitric Acid Electrolyte without Magnetic Field.—The test tube was filled with a 10 per cent. solution of HNO_3. The rheostat was set at 500 ohms, and electrodes immersed in solution, as in Fig. 1. The result of this experiment is best understood by following the curve in Fig. 2; the resistance introduced at the rheostat is represented by abscissa, the amperage passing through the circuit by ordinates. As the resistance was lessened from 500 ohms to 400, 300, and 200, the

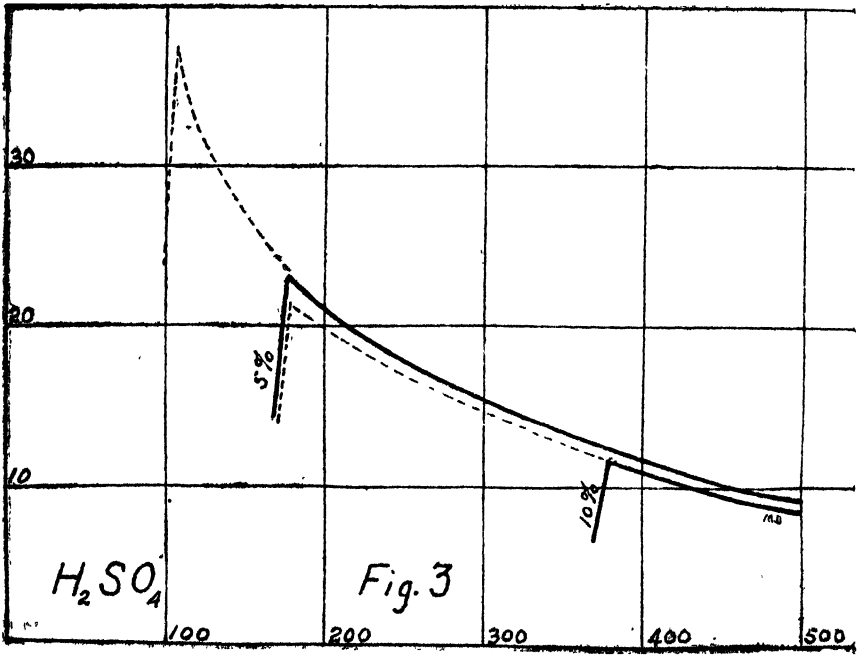


Fig. 3

amperage steadily increased till a point was reached at "A" when on removing 10 more ohms, the current dropped suddenly from 32.5 milliamperes to 20 milliamperes, marking the transition point from active to passive state, which is also shown by liberation of oxygen at the anode and a bright metallic surface of the iron.

In a Magnetic Field,—The above experiment was repeated in a magnetic field. Looking at the same curve (Fig. 2), the effect is readily seen; the transition point has been moved from *A* at 110 ohms resistance in rheostat, to *B* at 80 ohms. In other words, without the field, the sufficient and necessary strength of current to render the iron anode passive was 32.5 milliamperes; within a magnetic field, it would not become passive until the current had been raised to 40 milliamperes. This experiment with nitric acid was repeated many times, all results checking satisfactorily.

The above experiments were again repeated with a 5 per cent. solution of nitric acid. Here the effect of the magnet is even more marked (2), the transition point coming at *C* (45 milliamperes) without the field, and at *D* (65 milliamperes) within the field, a difference of 20 milliamperes. When the current through the electromagnet was stopped at any point between *D* and *C* (or in the former case between *B* and *A*) the iron *immediately* changed to the passive state, but once in this state the magnet was unable to restore it to the active condition. The only ways in which this could be done were by reducing the current

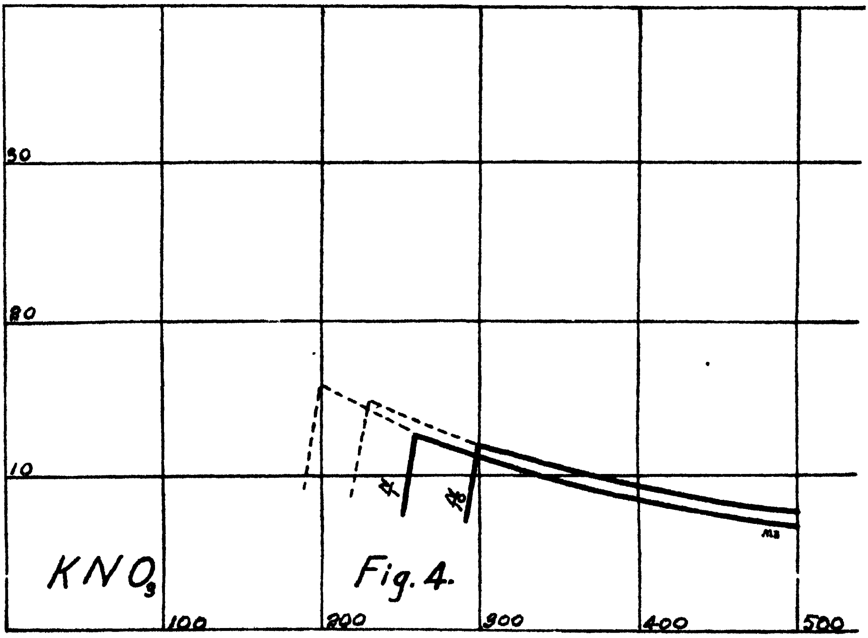
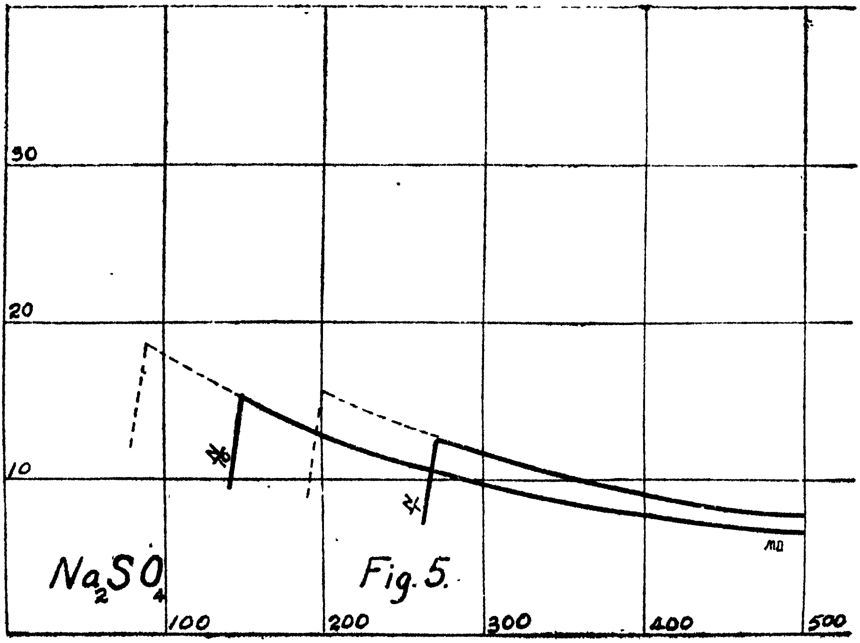


Fig. 4.

strength to a minimum with about 4000 ohms, by breaking the current, by bringing the electrodes into contact within the solution. This second transition point from *passive to active*, at about 4000 ohms was sharp, but difficult to measure accurately, and all efforts failed to show definitely whether it was affected by the magnetic field.

Results with Other Substances.—Using solutions of sulphuric acid instead of nitric acid, the four curves in Fig. 3 were plotted. They are of the same general nature as the nitric acid curves and illustrate well the effect of the magnet. Figs. 4 and 5 show the effect of the magnetic field on potassium nitrate and sodium sulphate solutions, respectively; in neither case is it nearly as great as for the active acids, but clearly of the same character. Fig. 6 is for phosphoric acid solutions. Here the effect of the magnet is greater than for the salts, but not as great as for the active acids. Similar experiments were made, using sodium hydroxide, potassium dichromate, dipotassium phosphate and monopotassium phosphate. Under all conditions solutions of the first three substances rendered the iron passive. In the case of a normal solution of monopotassium phosphate, however, by careful manipulation, the transition from active to passive iron could be found. However, this electrolyte did not behave as any one of the others, seeming to have properties akin to both the two opposite classes of electrolytes represented by sodium hydroxide and nitric acid, respectively. Although iron could be rendered active in this



solution, it would pass into the passive state within a considerable range of current density or by simply a short lapse of time. No effect of the magnetic field could be measured with this solution. With a 0.1 N solution, the passive properties were still more marked, so much so, that it could not be rendered active even temporarily. This is, of course, due to the hydrolysis of the salt. Two facts, which must be noted in connection with each of these passivity phenomena are: in no case, were any of the results affected in any way by the direction of the current through the electromagnet or by the relative positions of poles and electrodes; in no case, did the magnet cause a change in the amount of current passing through the electrolyte, or in the relative potentials of the two electrodes.

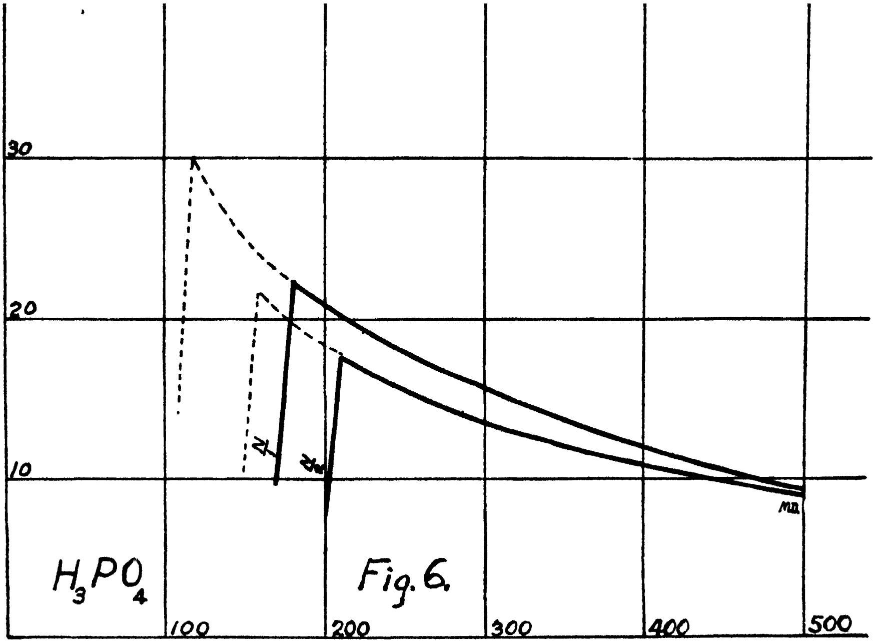


Fig. 6.

Conclusion.—In solutions of nitric, sulphuric and phosphoric acids, also of nitrates and sulphates, the transition point of passive iron to active iron is a function of current density but the transition is retarded by the magnetic field. It is of course recognized that passivity is also a function of temperature and concentration, but in these experiments they are constants and the only variables are current density and magnetic flux.

In the article previously referred to,[1] the writer gave a résumé of the various views in regard to passivity and stated that "none of them are satisfactory but that when experimental development warrants it he confidently expects the cause of passivity to be found to be an altered state of the metal itself, being produced by any one of several agents." The above experiments coupled with those of Nichols and Franklin seem to show that this altered state may be analogous to that of a number of magnets, the negative poles of which are all presented to the electrolyte, this orientation being produced by the various agents which cause the passive state. This view is not presented as proved but is tentative, and may lead to better work in this direction.

---

[1] THIS JOURNAL, 30, 1718 (1908).

UNIVERSITY OF WASHINGTON

THE INFLUENCE OF CHLORINE UPON THE DETERMINATION OF NITRIC NITROGEN.

BY ROBERT STEWART AND J E GREAVES

Received April 9, 1910

It is known that chlorine has an appreciable effect upon the determination of nitric nitrogen by the phenyldisulphonic acid method. Very little information, however, is available as to the amount of chlorine which may be present and not affect the reliability of the results. In connection with the study of the influence of irrigating water upon the movement and production of nitric nitrogen in the soil, this question was investigated quite thoroughly in this laboratory.[1] The results are of interest to others working along similar lines and also to chemists who are working with problems in sanitary water supply.

The chlorine in the soil under consideration was determined as follows: An aliquot portion of the extract of the soil, prepared as for the nitric nitrogen determination, was titrated against a one-hundredth normal silver nitrate solution. The results obtained are given in Table I. The results are expressed as parts of chlorine per million parts of soil.

TABLE I.—AMOUNT OF CHLORINE PRESENT IN THE SOIL EXTRACT

	Depth of soil in feet									
No of plot	1	2	3.	4	5	6.	7	8	9	10.
41 G.	0.849	0.814	0.496	0.923	0.567	0.779	0.744	0.673	0.815	0.496
42 G.	0.886	0.779	0.697	0.838	0.795	0.602	0.567	0.602	0.673	0.496
43 G.	0.780	0.425	0.921	0.709	1.134	0.496	0.922	0.496	0.425	0.425

These results indicate quite clearly that the chlorine in the soil under consideration did not exceed 1.134 parts per million.

It was then necessary to determine whether this amount of chlorine would interfere with the determination of nitric nitrogen by the phenyldisulphonic acid method. With this object in view, varying amounts of sodium chloride were added to given quantities of the standard potassium nitrate solution. The nitric nitrogen was then determined in the usual way. The results are very interesting and will be found in Table II. The results are expressed as parts per million.

---

[1] Utah Experiment Station, *Bull.* 106, p. 80.

TABLE II.—THE EFFECT OF CHLORINE ON THE SENSITIVENESS OF THE METHOD.

Chlorine added.	Nitric nitrogen present	Nitric nitrogen found.	Chlorine added.	Nitric nitrogen present.	Nitric nitrogen found
0.5278	0.1	0.1	5.278	0.1	0.1
1.056	0.1	0.1	5.886	0.1	0.095
1.584	0.1	0.1	6.342	0.1	0.094
2.113	0.1	0.1	6.856	0.1	0.092
2.638	0.1	0.095	7.362	0.1	0.092
3.167	0.1	0.090	7.917	0.1	0.092
3.694	0.1	0.098	8.446	0.1	0.092
4.224	0.1	0.090	8.9776	0.1	0.090
4.749	0.1	0.090	9.496	0.1	0.086

Similar determinations were made until a concentration of thirty parts per million of chlorine was reached. No further decrease in the amount of nitric nitrogen found was obtained, *i. e.*, the amount of nitric nitrogen found tended to approach a constant value of nine-tenths of the amount actually present.

The results show that chlorine, when present in quantities as low as 2.638 parts per million, affects the results for nitric nitrogen obtained by this method, less nitric nitrogen being found than is really present.

CHEMICAL LABORATORY, UTAH EXPERIMENT STATION

ON A NEW VOLUMETRIC METHOD FOR COBALT AND NICKEL.

BY GEORGE S. JAMIESON

Received April 8, 1910

The well-known application of potassium ferrocyanide to the volumetric determination of lead and zinc has led the writer to investigate the application of this method to the determination of cobalt and nickel, and conditions have been found under which concordant and accurate results may be obtained. As far as can be found by consulting the literature, this method has not been previously suggested.

It is believed that the most important practical application of the method will be in the determination of nickel in steel, for it can be carried out in the presence of iron, it is rapid and requires no expensive reagents. As far as ease and rapidity are concerned, it appears that the cyanide method as applied in the presence of iron by C. M. Johnson[1] and also by Campbell and Arthur[2] is the only one which can compete with it. The writer has found that by combining the modifications of the authors just referred to, the cyanide method may be decidedly improved, as will be shown by the description and the results which are given beyond. The choice between the ferrocyanide and the cyanide methods for nickel in steel would depend upon the preference of the operator, but it is to be observed that the cyanide method is not applicable to large amounts of cobalt on account of a peculiar dark precipitate produced under these circumstances during the cyanide titration which interferes with the end reaction.

---

[1] THIS JOURNAL, 29, 1201 (1907).

[2] *Ibid.*, 30, 1116 (1908).

For the ferrocyanide titration a solution containing 20 grams per liter of potassium ferrocyanide is recommended as a suitable strength for most work. Then each cubic centimeter will be equivalent to about 3 milligrams of cobalt or nickel. To standardize this it is best to employ a cobalt or nickel solution of known strength prepared either from pure salts in known volume, or by gravimetric standardization. Three equal portions of this solution containing about 0.1 gram of the metal are taken in beakers. Ten cc. of a 10 per cent. solution of ferric chloride and 2 to 3 grams of citric acid are added to each and then ammonia is added with stirring until the solution has a faint odor of the reagent. It is important that the excess of ammonia should not be too great, as in this case the results will be irregular. The solutions are then diluted to about 100 cc. with hot water and are brought to a temperature of 65–75°. The ferrocyanide solution is now run in slowly with constant stirring. After a few drops of the ferrocyanide have been added, the nickel or cobalt ferrocyanide begins to precipitate. As the titration progresses, a drop or two of the solution is removed by means of the stirring rod to a paraffined white plate and acidified with a drop of dilute acetic acid. The solution is thoroughly stirred and a second test is made in the same way beside the other. This pair of tests is designated as No. 1 and a record is made of the volume of ferrocyanide used at this point. The titration is carried on in this way until a greenish color is developed in about five minutes at a definite point in the series. The most convenient practice is to titrate the first portion roughly, and then to get the exact point with the other two portions. The important precautions are to avoid more than a slight excess of ammonia and to titrate slowly with thorough stirring.

The actual determinations are made in exactly the same way as the standardization just described. The method cannot be applied in the presence of such metals as copper, zinc, and manganese which react with potassium ferrocyanide. In the case of substances containing a considerable amount of iron, which must be in the ferric condition, no addition of ferric chloride is required.

The following results were obtained with varying quantities of cobalt and nickel solutions:

The following directions may be followed for the determination of nickel in steel: Weigh out 1.0000 gram of borings into a 150 cc. flask, add 10–15 cc. of dilute nitric acid (equal volumes of 1.42 sp. gr. acid and water). Cover the flask with an inverted crucible cover, and when the violent action is over, remove cover and boil gently over a free flame, keeping the flask in constant motion and inclined at about 45°, until the

1 cc. $K_4Fe(CN)_6$ soln. = 0.002105 gram Co, or 0.001885 Ni.

No	Co taken. Gram.	cc. $K_4Fe(CN)_6$ used.	Co found. Gram.	Error.
1	0.0632	30.1	0.0633	+0.0001
2	0.0379	18.0	0.0379	±0.0000
3	0.0379	18.0	0.0379	±0.0000
4	0.0063	3.1	0.0065	±0.0002
5	0.0442	21.0	0.0442	±0.0000
6	0.0505	24.0	0.0505	±0.0000
7	0.0537	25.7	0.0541	+0.0004
8	0.0287	13.5	0.0284	—0.0003
9	0.0144	4.6[1]	0.0145	+0.0001
10	0.0144	4.6[1]	0.0145	+0.0001
	Ni taken		Ni found	
11	0.0462	24.5	0.0462	±0.0000
12	0.0770	40.8	0.0769	—0.0001
13	0.0770	40.8	0.0769	—0.0001
14	0.0377	19.8	0.0373	—0.0004

steel is decomposed. (If a steel is encountered which is not entirely dissolved by nitric acid, add a drop or two of strong hydrochloric acid or a crystal of potassium chlorate and continue the boiling.) Add 10 cc. of concentrated nitric acid as soon as the steel is in solution, heat to boiling again, and add half a gram of solid potassium chlorate. Boil until the chlorine is expelled. Add the same quantity of chlorate again and boil for about two minutes. Then allow the flask to cool a little and filter off the manganese dioxide on a Gooch crucible, washing with as small a quantity as possible of cold water. Proceed then according to the method already described. It is to be observed that the presence of a large amount of iron, as in the case of nickel steel, somewhat retards the appearance of the end reaction. It is advisable to standardize the ferrocyanide solution in the presence of about the same amount of iron as is present in 1 gram of steel. The following determinations were made in the three samples of steel by the method just described. The nickel in A was checked by the electrolytic, ether-cyanide, and dimethyl-glyoxime methods. The analyses of samples B and C were completed before the results by other methods were known.

No.	Ni steel. Grams	cc. $K_4Fe(CN)_6$.	Per cent nickel.	Ni by other methods
1A	1.0000	11.55	3.63	3.65
2A	1.0000	11.50	3.62	3.65
3A	1.0000	11.60	3.64	3.65
1B	1.0000	11.00	3.46	3.47
2B	1.0000	10.90	3.43	3.47
3B	1.0000	11.10	3.49	3.47
4B	1.0000	11.10	3.49	3.47
1C	1.0000	11.20	3.52	3.50
2C	1.0000	11.10	3.49	3.50
3C	1.0000	11.20	3.52	3.50

[1] Another ferrocyanide solution.

Duplicate analyses of nickel in a steel can be made in this way in about an hour, and the results show that the method is accurate.

The following application of the cyanide method to the determination of nickel in steel was worked out by the writer before the papers of Johnson and Campbell and Arthur, which have been previously referred to, had been seen. The former investigator used a large amount of citric acid, while the latter used a large amount of sodium pyrophosphate. The writer uses both of these reagents together, but in much smaller quantity. The directions, according to the writer's modification, are as follows:

Take 0.5 gram of borings in a 150 cc. flask, add 10 cc. of 1 : 1 nitric acid and dissolve according to the directions given for the ferrocyanide method. If the metal contains more than 0.5 per cent. of manganese, the writer prefers to remove it according to the directions just referred to. Add to the nitric acid solution 2 to 3 grams of citric acid and 2 grams of anhydrous sodium pyrophosphate, then add ammonia slowly with stirring until the precipitate formed at first just dissolves and the solution acquires a very faint odor of ammonia. If too much ammonia has been used, it must be nearly neutralized by the careful addition of nitric acid. Dilute to about 150 cc. and cool to a temperature below 20°, add a few drops of a 10 per cent. solution of potassium iodide, and enough tenth-normal silver nitrate solution, the volume of which must be noted, to produce a distinct turbidity. Then run in potassium cyanide solution very slowly with stirring until the turbidity just disappears and the solution lightens to a golden yellow color. The solution should remain bright for five minutes, otherwise the titration is incomplete. Sometimes it happens that the turbidity disappears when only one-third to one-half of the required amount of cyanide has been used, but in this case upon the addition of a drop or two of silver nitrate, or upon waiting a moment, the turbidity reappears. The end-point is best observed when the beaker is placed upon a white paper having an elliptical hole in it under which is placed a black glazed paper for contrast. In making the calculation the proper deduction for the silver nitrate used should be made.

The potassium cyanide solution should be standardized by means of the tenth-normal silver nitrate. To do this take 20 cc. in a beaker, dilute to about 150 cc. with cold water, add ammonia until the odor is distinct but slight, add a few drops of 10 per cent. potassium iodide solution, run in silver nitrate until a distinct turbidity is produced, and then finish by slowly adding the cyanide solution until the turbidity just disappears. The theoretical amount of nickel per 1 cc. of tenth-normal solution is 0.002935 gram, but instead of using this value it is perhaps preferable to standardize the solution with a steel of known content in nickel.

The theoretical value was used in the test analyses given below, which indicate very satisfactory results for the method.

No	Ni steel Gram.	cc. KCN	Per cent. nickel.	Ni by other methods
1A.	0 5000	6.70	3.70	3.65
2A.	0 5000	6.62	3 67	3.65
3A	0.5000	6.60	3.66	3.65
1B.	0 5000	6 25	3 46	3.47
2B	0 5000	6 26	3.48	3.47

SHEFFIELD LABORATORY, NEW HAVEN, CONN

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON AMINES: ALKYLATIONS WITH DIMETHYLSULPHATE. SYNTHESIS OF DIMETHYLPHENYLETHYLAMINE.

(THIRD PAPER.)

BY TREAT B JOHNSON AND HERBERT H. GUEST.

Received March 23, 1910

Contents.—1. Historical. 2. Purpose of Investigation and Discussion of Results. 3. Experimental Part.

1. Historical.

That dialkylsulphates (dimethyl- and diethylsulphates) can be used in place of the corresponding halides for the alkylation of amines has been known for a long time. Dumas and Peligot,[1] in 1835, examined the behavior of dimethylsulphate towards ammonia and observed the formation of methylalcohol and methylammonium sulphate (Sulfomethylan). Strecker[2] repeated this experiment and also investigated the action of diethylsulphate on ammonia. He found that the reactions were not as simple as assumed by Dumas and Peligot and obtained, with diethylsulphate, the ammonium salt of an acid, $C_{16}H_{23}NO_4.4SO_3 + NH_3$ (athylaminschwefelsäure Ammoniak), from which he prepared ethylamine by decomposition with alkali.

Babo[3] examined the action of dimethylsulphate (Schwefelsaures Methyloxyd) on aniline and showed that it alkylated smoothly giving monomethylaniline. He also observed that quinoline and nicotine reacted with this reagent and diethylsulphate giving crystalline addition products (quaternary compounds?).

The study of the action of these sulphates on amines received no further attention, apparently, until 1880 when a paper by Claesson and Lundvall[4] appeared, in which they describe their behavior towards ammonia and several aliphatic and aromatic bases. They repeated the work of Strecker and observed that diethylsulphate reacted with ammonia giving not only ethylamine, but also the quaternary salt $(C_2H_5)_4N.SO_4C_2H_5$. Quaternary salts were also obtained by alkylation of diethylamine, dimethylaniline and tribenzylamine with dimethylsulphate. They write: "Die Reaktion zwischen Ammoniak und Methylsulfat ist somit eine rein additionelle. Sie verläuft nach folgender Gleichung:

---

[1] *Ann. chim. phys.*, 58, 32.

[2] *Ann.*, 75, 46.

[3] *J. pr. Chem.*, [1] 72, 84 (1857); *Chem. Centr.*, 218 (1858).

[4] *Ber.*, 13, 1700.

$$CH_3OSO_2OCH_3 + NH_3 = CH_3OSO_2ONH_3.CH_3."$$

The usefulness of dimethylsulphate as an alkylating agent for amines was later greatly enhanced by the work of Ullmann and his co-workers.[1] They showed that it not only reacted smoothly with organic bases (in ether, chloroform and benzene), but also that it can be employed successfully for the alkylation of cyclic amines, *viz.*: quinolines, aminonaphthacridines, phenylacridines, diaminoacridines and aminophenazines. They write:[2] "Die Resulte übersehen lassen, dass Dimethylsulfat in allen Fällen das Iodmethyl ersetzen kann, aber meistens noch bedeutend rascher und besser als dieses reagirt." Ullmann's[3] interpretation of the reactions between amines and dimethylsulphate is summarized in his own words—"Dieselbe verläuft nämlich nicht, wie Claessón und Lundvall augegeben,—Es entsteht also das methylschwefelsäure primäre Amin und die entsprechende secundäre Base."

$$(CH_3)_2SO_4 + 2RNH_2 = RNH_2.H.CH_3SO_4 + RN\overset{\cdot}{H}CH_3.$$

Decker and his students[4] have used the alkylsulphates for the preparation of quaternary derivatives of cyclic bases. For example, they were unable to obtain quaternary compounds of several quinolines by addition of methyliodide, while, on the other hand, dimethylsulphate reacted quantitatively giving the corresponding quaternary alkyl sulphates. Methyldiphenylamine reacted smoothly with dimethylsulphate at 140–150° giving the quaternary compound $(C_6H_5)_2(CH_3)_2NSO_4CH_3$[5] while no addition took place with methyliodide under the same conditions.

The action of dimethylsulphate on the glyoxaline ring was studied by Pinner.[6] He examined its behavior towards diphenylglyoxaline I, and triphenylglyoxaline (Lophine) II, but did not observe the formation of nitrogen methyl derivatives. Lophine reacted abnormally with the sulphate giving a characteristic double compound, $C_{21}H_{16}N_2.(CH_3)_2SO_4.2H_2O$, having the properties of a salt. Pinner remarks that the sulphate acts in this case as a weak acid and that the compound has not the possible structure of a quaternary compound III (Methylschwefelsaures Methyllophin). He writes: "Es ist nicht ohne Interesse, das Verhalten von Methylsulfat anderen Basen gegenüber zu untersuchen."

---

[1] Ullmann and Naef, *Ber.*, 33, 2470 (1900); Ullmann and Wenner, *Ibid.*, 33, 2476; Ullmann and Marié, *Ibid.*, 34, 4307 (1901); Ullmann, *Ann.*, 327, 104 (1903).

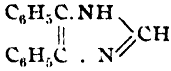
[2] Ullmann and Wenner, *Loc. cit.*

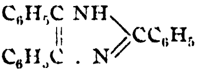
[3] *Ann.*, 327, 107.

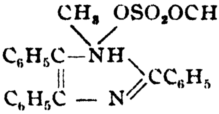
[4] *Ber.*, 36, 261 (1903); 38, 1147, 2493; Decker and Schenck, *Ibid.*, 39, 748; Schmid and Decker, *Ibid.*, 39, 933 (1906).

[5] Gadomska and Decker, *Ber.*, 36, 2487 (1903).

[6] *Ber.*, 35, 4141 (1902).


I.


II.


III.

Bamberger[1] employed dimethylsulphate for the preparation of *o*-monomethyl- and *o*-dimethylaminobenzaldehydes from *o*-aminobenzaldehyde and also later for the alkylation of mesidine to monomethyl- and dimethylmesidines.[2] This reagent has also been used successfully for the alkylation of amino compounds by Johnston,[3] Baeyer,[4] Willstatter and Kahn,[5] Weil,[6] Smith,[7] Burmann,[8] Frohlich,[9] and Houben and Brassert.[10]

In no case, so far as the writer is aware, has it been observed that an amine can react with dimethylsulphate, in a similar manner as with an aliphatic ester, giving an amide of sulphuric acid. It is interesting to note in this connection that recent attempts by Ephraim and Gurewitch[11] to prepare sulfamide $SO_2(NH_2)_2$ from dimethylsulphate by action of ammonia, in alcohol solution and in liquid form, were unsuccessful. They reacted, under both conditions, with formation of methylamine according to the following equation:

$$SO_2(OCH_3)_2 + 2NH_3 = CH_3OSO_2ONH_4 + NHCH_3.$$

2. Purpose of Investigation and Discussion of Results.

The work described in this paper was undertaken with the object of determining the behavior of dimethylsulphate towards some aromatic β-amines.

Any methods, by which the nitrogen alkyl derivatives of phenylethylamine IV, or *p*-hydroxyphenylethylamine V, can be obtained easily are of value, on account of the interest, at the present time, of compounds of this character to pharmacologists. Of all the nitrogen alkyl derivatives of phenylethylamine, dimethylphenylethylamine, VII, is probably the the most interesting because of its close structural relationship to the naturally occurring alkaloid *hordenine*, VIII (dimethyl-*p*-hydroxyphenylethylamine). It seemed desirable therefore, to the writer, to determine whether this base, VII, can be synthesized by direct alkylation of phenylethylamine. Previous attempts to prepare it by alkylation of the latter with methyliodide have been unsuccessful.

---

[1] *Ber.*, **37**, 966 (1904).

[2] Bamberger and Rudolf, *Ibid.*, **39**, 4285 (1906).

[3] *Proc. Chem. Soc.*, **21**, 156; *Chem. Centr.*, **1905**, II, 44; *Proc. Roy. Soc.* (London), **78**, 82; *Chem. Centr.*, **1906**, II, 1006.

[4] *Ann.*, **354**, 152.

[5] *Ber.*, **37**, 408 (1904).

[6] *Monatsh.*, **29**, 875.

[7] *J. Chem. Soc.*, **89**, 1505 (1906).

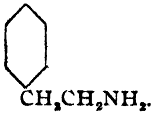
[8] *Bull. soc. chim.*, [3] **35**, 801 (1906).

[9] *Ber.*, **42**, 1561 (1909). For further works on alkylation of amines with alkylsulphates see: D. R. P. 79703 (1895). D. R. P. 102634. *Chem. Centr.*, **1899**, II, 408 (Merck). D. R. P. 131758. *Ibid.*, **1902**, I, 1385. D. R. P. 134176. *Ibid.*, **1902**, II, 775 (Farbenfabriken vorm. Friedr. Bayer & Co.); Berger, *Diss. Leipzig* (1904); Feuerlein, *Diss. Zurich* (1907).

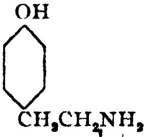
[10] *Ber.*, **43**, 206.

[11] *Ibid.*, **43**, 139 (1910).

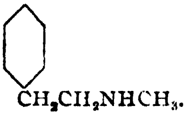
Johnson and Guest[1] showed in a paper from this laboratory that methyliodide reacts with phenylethylamine giving the hydriodide of the unaltered base and the quaternary derivative—*trimethyl-phenylethylammonium-iodide*. No matter what proportion of the methyliodide was used, they obtained no evidence of the formation of monomethyl- or dimethylphenylethylamines, VI and VII. This observation was later confirmed by Barger.[2]



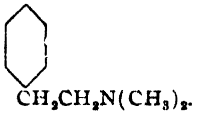
IV.



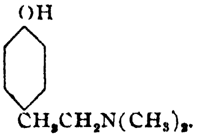
V.



VI.



VII.



VIII.

We now find that this base, VII, can be prepared from phenylethylamine by alkylation with dimethylsulphate. Several negative experiments, however, were performed before we finally succeeded in obtaining conditions favorable for its formation. All attempts to alkylate in aqueous solution, in the presence of alkali, were unsuccessful. The action of dimethylsulphate, in ether, was also investigated, but the results were similar to those obtained in our alkylation experiments with methyliodide. The products of the reaction were the phenylethylamine salt of methylsulphuric acid and a hydroscopic salt having the properties of a quaternary derivative. Conversion into the tertiary base was finally accomplished by alkylation, in methyl alcohol, in the presence of sodium methylate. In this manner a good yield of the base was obtained, which boiled at 200–204° at ordinary pressure.

This same amine (b. 198–202°) has also recently been prepared by Barger[3] by heating phenylethylchloride with dimethylamine, but so little

[1] *Am. Chem. J.*, 42, 340.

[2] *J. Chem. Soc.* (London), 95, 2194.

[3] *Loc. cit.*

material was obtained by him that it was not analyzed nor well characterized. Since he showed that the base gives, by nitration at —10°, a good yield of the paranitro derivative IX (60 per cent.), which can be converted into a base identical with *hordenine*, our synthesis of the amine VII therefore offers a method of preparing *hordenine* directly from phenylethylamine.

$$C_6H_5CH_2CH_2NH_2 \longrightarrow C_6H_5CH_2CH_2N(CH_3)_2 \longrightarrow$$
$$\underset{\text{IX.}}{NO_2C_6H_4CH_2CH_2N(CH_3)_2} \longrightarrow HOC_6H_5CH_2CH_2N(CH_3)_2$$

The interesting behavior of phenylethylamine towards dimethylsulphate led us to examine also the action of this reagent on *p*-nitrophenylethylamine.[1] To our surprise, this base underwent no alkylation, in methyl alcohol, in the presence of sodium methylate and practically 90 per cent. of the amine used was recovered unaltered. It was identified by its hydrochloride, and on reduction was converted smoothly into *p*-aminophenylethylamine.[2]

This difference between phenylethylamine and *p*-nitrophenylethylamine, in their behavior towards dimethylsulphate, is probably due to the fact that one is a much stronger base than the other. Phenylethylamine, being the most basic, adds dimethylsulphate at once, and undergoes alkylation before the sulphate is decomposed by the sodium methylate. On the other hand, *p*-nitrophenylethylamine, which is the weaker base on account of the negative influence of the *p*-nitro group, has a much less tendency to add the sulphate, under the conditions of the experiment; consequently the latter is completely decomposed by the sodium methylate and the amine is recovered unaltered. Dimethyl sulphate would be expected to react readily with sodium methylate, in a similar manner as with methyliodide, giving dimethyl ether and the sodium salt of methylsulphuric acid or sodium sulphate,

$$CH_3OSO_2OCH_3 + NaOCH_3 = CH_3OSO_2ONa + (CH_3)_2O,$$

or

$$CH_3OSO_2OCH_3 + 2NaOCH_3 = Na_2SO_4 + 2(CH_3)_2O.$$

That our assumption is correct is supported by the fact that the odor of dimethyl ether was apparent during the reaction, and also by a previous observation of Nef.[3] He showed, for example, that dimethylsulphate is decomposed practically quantitatively when dissolved in a cold methyl alcohol solution of potassium hydroxide, giving dimethyl ether and potassium sulphate.

Attempts to prepare secondary and tertiary amines from *p*-nitrophenylethylamine by alkylation with methyliodide were also unsuccessful.

---

[1] Johnson and Guest, *Am. Chem. J.*, 43.

[2] Johnson and Guest, *Loc. cit.*

[3] *Ann.*, 309, 186 (1899).

They reacted at 100°, in methyl alcohol, giving the hydriodide of the unaltered base and *trimethyl-p-nitrophenylethylammonium iodide.*

The writers[1] have shown that acetyl-*p*-nitrophenylethylamine can be obtained in good yield by nitration of acetylphenylethylamine. We now find that the corresponding methyl derivative of this nitro amide, XI, can be prepared, in a similar manner, by nitration of acetylmethylphenylethylamine, X. It was converted quantitatively into the unknown *p*-nitrophenylethylmethylamine, XII, by hydrolysis with acids.

$$C_6H_5CH_2CH_2NH_2 \longrightarrow C_6H_5CH_2CH_2NHCH_3 \longrightarrow$$

$$\underset{\text{X.}}{C_6H_5CH_2CH_2N(CH_3)COCH_3} \longrightarrow \underset{\text{XI.}}{NO_2C_6H_4CH_2CH_2N(CH_3)COCH_3} \longrightarrow$$

$$\underset{\text{XII.}}{NO_2C_6H_4CH_2CH_2NHCH_3}.$$

3. Experimental Part.

Action of Dimethylsulphate on Phenylethylamine in Ether.—Five grams of the amine were dissolved in ether and 20 grams of the sulphate (8 mols.) added slowly to the solution. There was an immediate reaction with evolution of heat and about 10 grams of a colorless crystalline salt separated. After allowing to stand for an hour, this was filtered off and the ether filtrate allowed to evaporate. We obtained an oil (mostly unaltered dimethylsulphate) to which was added an excess of alkali and then subjected to steam distillation. No bases were carried over by the steam. A portion of the material, insoluble in ether, was purified by dissolving in alcohol and then precipitating by dilution with ether. Glistening plates separated and melted at 75–77° to an oil. A nitrogen determination indicated that the substance was the *phenylethylammonium salt of methylsulphuric acid,* $C_6H_5CH_2CH_2NH_3.SO_4CH_3$.

Calculated for $C_9H_{15}O_4NS$: N, 6.0; found: N, 5.55.

The remainder of the salt was shaken with an excess of ether and in presence of a strong aqueous solution of sodium hydroxide. A crystalline product remained undissolved by this treatment. It was soluble in cold water and alcohol and could be warmed in sodium hydroxide solution without decomposition. The compound was very hydroscopic, contained sulphur and decomposed from 100–110° with effervescence. Its chemical behavior indicated that it was a quaternary salt.

Phenylisothiocyanate was added to the ether solution above and the ether allowed to evaporate in the air. Beautiful prisms of 1-phenyl-2-phenylethylthiourea finally separated and melted, after one crystallization from alcohol, at 106°. A mixture of this compound and some of the pure thiourea prepared from phenylethylamine melted at the same temperature.

Dimethylphenylethylamine, $C_6H_5CH_2CH_2N(CH_3)_2$.—Eight and four-tenths grams of metallic sodium (3 at.) were dissolved in 135 cc. of methyl alcohol and 14.5 grams of phenylethylamine added to the solution. Kahlbaum's dimethylsulphate (46 grams) was then added, in small portions, when there was a violent reaction with evolution of heat and separation of a gelatinous salt. After the final addition of dimethylsulphate, 50 cc. of methyl alcohol were added and the mixture heated on the steam bath for about 5 hours. It was then acidified with hydrochloric acid and evaporated to dryness to remove the excess of alcohol and acid. In order to separate the base, the hydrochloride was decomposed with an excess of sodium hydroxide and the bases distilled with steam and dissolved in hydrochloric acid. On evaporating to dryness a hydroscopic salt was obtained, which was dissolved in 75–100 cc. of cold water and treated with an excess of potassium nitrite, for about 10 minutes, to remove any primary and secondary amines. An excess of alkali was then added and the tertiary amine extracted with ether and dried over potassium hydroxide. It is a strong base which absorbs carbon dioxide from the air and boils at 200–205° at ordinary pressure. The yield was good.

---

[1] *Loc. cit.*

Calculated for $C_{10}H_{15}N$: N, 9.40; found: N, 9 38.

Platinum Salt.—Crystallizes from water in hexagonal tables which decompose at 221°. A mixture of this salt and the corresponding salt of methylphenylethylamine[1] (m. 212°) melted below 207°.

Hydrochloride, $C_6H_5CH_2CH_2N(CH_3)_2.HCl$.—This salt was prepared by dissolving the base in dilute hydrochloric acid and then allowing the solution to evaporate in a vacuum over potassium hydroxide. The salt separated under these conditions in colorless plates, which melted at 205° to an oil. It decomposed with effervescence when heated above 270°.

Acetylmethylphenylethylamine, $C_6H_5CH_2CH_2N(CH_3)COCH_3$.—This amide was prepared by carefully adding 15 grams of freshly distilled thioacetic acid to 19 grams of methylphenylethylamine[1] and then heating at 210° for 1–2 hours to complete the reaction. The amide was a dark-colored oil, which did not solidify after standing at ordinary temperature for several hours. It was used for the following preparation without further purification.

Acetylmethyl-p-nitrophenylethylamine, (*p*) $NO_2C_6H_4CH_2CH_2N(CH_3)COCH_3$.—This compound was prepared by dissolving 25 grams of acetylmethylphenylethylamine in 85 cc. of nitric acid (sp. gr. 1.51). The temperature was not allowed to rise above 5° during the nitration. After allowing to stand for a few minutes the solution was then diluted with ice water and the nitric acid neutralized with ammonia when the amide separated as an oil. This was extracted with ether and the ether solution allowed to evaporate spontaneously when the amide finally solidified. More separated from the aqueous filtrate on standing. The crude substance melted at 90–94°.

---

[1] Johnson and Guest, *Loc. cit.*

The amide is very soluble in ethyl acetate, ethyl alcohol, chloroform and benzene. It was purified for analysis by several recrystallizations from ethyl acetate and a mixture of petroleum ether and benzene. It melted at 100–101° to a clear oil without effervescence (Kjeldahl):

Calculated for $C_{11}H_{14}O_3N_2$: N, 12.6; found: N, 12.10.

Oxidation of Acetylmethyl-p-nitrophenylethylamine with Potassium Dichromate.—About 0.9 gram of this amide and 3.2 grams of potassium dichromate were dissolved in 6.5 cc. of concentrated sulphuric acid and the solution heated at 60° for about 10–12 hours. A crystalline acid was obtained, which crystallized from hot water in prismatic crystals, and melted, after purification, at 234°. It was identified as paranitrobenzoic acid. A mixture of our acid and paranitrobenzoic acid melted at the same temperature.

Methyl-p-nitrophenylethylamine, (*p*) $NO_2C_6H_4CH_2CH_2NH(CH_3)$.—This amine was obtained, in the form of its hydrobromide, when the above acetyl derivative was digested with hydrobromic acid. The base separated as a heavy, yellow oil when sodium hydroxide was added to an aqueous solution of the hydrobromide.

1-Phenyl - 2,2 - methyl - p - nitrophenylethylthiourea, (*p*) $NO_2C_6H_4CH_2CH_2N(CH_3)CSNHC_6H_5$.—This thiourea was prepared by the action of phenylisothiocyanate on the above methyl-*p*-nitrophenylethylamine. It crystallizes from 95 per cent. alcohol in plates, which melt at 137–138°. A mixture of this thiourea and 1-phenyl-2-paranitrophenylethylthiourea[1] melted at 109–115° (Kjeldahl):

Calculated for $C_{16}H_{17}O_2N_3S$: N, 13.3; found N, 12.8.

Action of Dimethylsulphate on Paranitrophenylethylamine, $NO_2C_6H_4CH_2CH_2NH_2$.—Nine and two-tenths grams of the hydrochloride of *p*-nitrophenylethylamine[1] were dissolved in 50 cc. of methyl alcohol containing 3.7 grams of sodium. Fourteen and three-tenths grams of dimethylsulphate, boiling at 104–110° at 28–30 mm., were then added slowly to the cooled solution by means of a dropping funnel. There was an immediate reaction with evolution of much heat. After the addition of dimethylsulphate the mixture was heated to boiling, allowed to stand for 2.5 hours, acidified with an excess of hydrochloric acid and finally concentrated on the steam bath. An excess of alkali was then added when unaltered *p*-nitrophenylethylamine separated. This was extracted with ether and dried over potassium carbonate. The yield was 6.0 grams. A theoretical yield of unaltered *p*-nitrophenylethylamine would be 7.0 grams. The hydrochloride melted at 213–214°.[1]

Reduction of the Nitrophenylethylamine to Paraaminophenylethylamine,[1] their studies. The first to compared with the reading of the neutral observed during this rea

---

[1] Johnson and Guest, *Loc. cit.*

macist of the eightee *in Various Acid Solutions.*—The measurements history of chemical e made in the manner described in the preceding with the theovalues are recorded in Table II.

Théorique ACTIVITY OF PURIFIED INVERTASE IN SOLUTIONS OF VARIOUS ACIDS.

it is the

orms

thi

	Acidity of invertase in the acids named.									
entration of acid (gram equivalents per liter)	Hydro-chloric	Nitric	Sulphuric	Phos-phoric	Hydro-bromic	Boric.	Oxalic.	Tartaric.	Citric.	Acetic.
Distilled water	4 8	4 5	4.5	5 8	4 3	5 0	9 0	9 0	13	15
0 00009	30	29	34		34	...	49	43	49	..
0 00012	.	....	..	27	.	....	..	. .	..	.
0 0005	62	61	62	.	59	. .	57	58	58	..
0 0007	.			59	..	. ..	..	.	.	..
0.0015	61	61	59		58	31	57	56	59	.
0 0021	.			62	..	...	. .	....	.	..
0 003	58	55	51	...	53	. ..	...	56	..	..
0.004	.	....		54	.	. .	55	.		.
0 008	37	28	19	....	31	45	46	54	56	.
0.010	(1)	(1)	(1)	.	(1)		. ..		..	57
0 011	(1)	(1)	(1)	(1)	(1)	. ..	.	. .	..	..
0.014	(1)	(1)	(1)	(1)	(1)	47	34	50	54	..
0.020	(1)	(1)	(1)	(1)	(1)	..	25	48	52	..
0.023	(1)	(1)	(1)	(1)	(1)	..	.		..	56
0 025	(1)	(1)	(1)	(1)	(1)	....	21	45	50	..
0.028	(1)	(1)	(1)	(1)	(1)	..	.	...	..	..
0 030	(1)	(1)	(1)	(1)	(1)	45	.	....	50	..
0 035	(1)	(1)	(1)	(1)	(1)	43	. .	..	48	..
0.040	(1)	(1)	(1)	(1)	(1)	41	....	....	46	..
0.045	(1)	(1)	(1)	(1)	(1)	35	....	....	45	..
0.072	(1)	(1)	(1)	(1)	(1)	. .	....	....	..	54
0.12	(1)	(1)	(1)	(1)	(1)	....	....	....	..	54
0.24	(1)	(1)	(1)	(1)	(1)	...	....	...	..	50
0.35	(1)	(1)	(1)	(1)	(1)	....	....	....	..	44
0.54	(1)	(1)	(1)	(1)	(1)	.. .	...	....	..	37
0 96	(1)	(1)	(1)	(1)	(1)	....	....	....	.	21

In Fig. 1 the curves for the five strong acids—hydrochloric, hydrobromic, nitric, sulphuric, and phosphoric—fall so closely together that one unbroken line is shown for them all. The enzyme begins to be destroyed by these mineral acids at a concentration of about 0.01 normal and the measurements of the activity were not made above this limit. The falling of the curve (Fig. 1) with increasing acidity shows a characteristic progression in the order, strong mineral acids, oxalic, tartaric, citric, acetic, and boric, which is also the order of the strengths of these

---

[1] Destruction of enzyme occurs.

acids. If the ionization of the acids is ta activity plotted against the actual hydrogen-i weaker acids all give curves agreeing closely mineral acids. The enzymotic activity is thus the hydrogen-ion concentration. The theoretical int characteristic relation between the activity and the true postponed until further investigations have been made.

The Destruction of Invertase by Acids and Alkalis at 30° C.—The tion of invertase by acids and alkalis at 30° was measured by mix portion of well dialyzed invertase solution with the appropriate acid alkaline solution, removing portions of this mixture after definite intervals of time and measuring their activities after bringing them to a uniform condition of slight acidity with acetic acid in order to find the maximum activity which is a measure of the quantity of invertase in the solution. If the activities of the successively removed samples showed a decrease it was concluded that the invertase was being destroyed by the acid or alkaline solution. The following typical experiment shows that the rate of this destruction follows the formula for unimolecular reactions, namely, $1/t \log A/A - x = k_2$, where A is the activity of the invertase at the beginning of the destruction, x is the activity after the destruction has proceeded for t minutes, and k_2 is a constant, the velocity coefficient. The concentration of acid in this experiment was 0.02 normal hydrochloric.

TABLE III.—THE UNIMOLECULAR ORDER OF THE DESTRUCTION OF INVERTASE.

Time Minutes	Activity (× 10000)	Rate of destruction (k_2).	Time Minutes	Activity (× 10000)	Rate of destruction (k_2).
0	50.5	.....	70	24.9	0.0044
25	39.0	0.0045	85	22.0	0.0042
40	33.1	0.0046	115	17.7	0.0040
55	28.4	0.0045	...	....	......

In Table IV the rate of destruction, that is, the velocity coefficient k_2 multiplied by 1000, is recorded for various strengths of hydrochloric acid and sodium hydroxide solutions at 30°, the results are also shown in Fig. 2.

TABLE IV.—RATE OF DESTRUCTION OF INVERTASE AT 30° BY ACID AND ALKALI.

Concentration (Gram molecules per liter.)	Rate of destruction of invertase (k_2 1000)	Concentration. (Gram molecules per liter.)	Rate of destruction of invertase (k_2 1000)
Normal hydrochloric acid:		Distilled water.........	0
0.05................	365	Normal sodium hydroxide:	
0.04................	96	0.01................	3
0.03................	42	0.02................	11
0.02................	4	0.03................	50
0.015...............	1	0.04................	245
0.01................	0		

Summary.

Acids and alkalis are found to affect the purified enzyme invertase

their studies. The first tontrations they influence its activity but do observed during this reit, in larger concentrations they accomplish macist of the eightee struction by acid at 30° reaches a barely noticeable history of chemical acidity and increases rapidly with the acidity until with the theorst instantaneous at 0.05 normal. The rate of destruction Théorique rmula for unimolecular reactions. The alkaline destruction it is the ttle below 0.01 normal and is almost instantaneous at 0.045 orm! The rates of destruction are shown in Fig. 2.
th

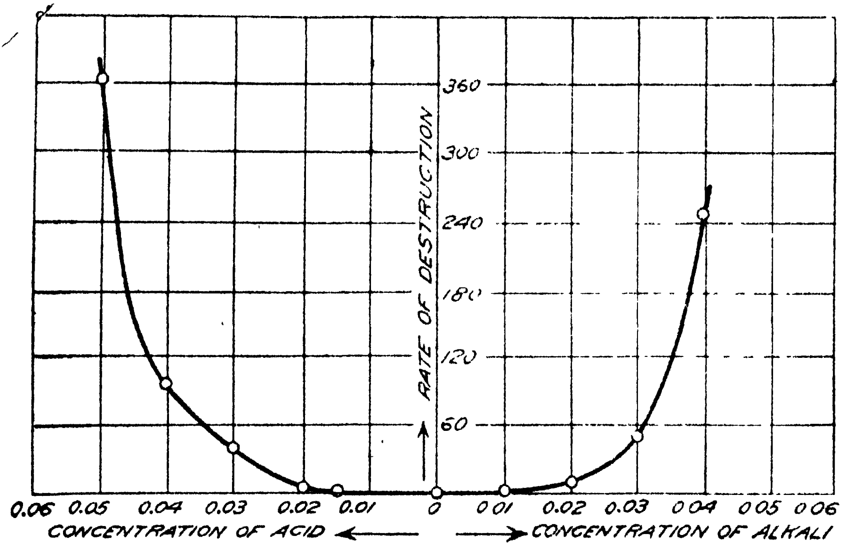


Fig. 2.—The rate of destruction of invertase at 30° C. by acid and alkali.

The activity of invertase in acid solutions which are not strong enough to destroy the enzyme was measured for hydrochloric, hydrobromic, nitric, phosphoric, sulphuric, boric, oxalic, tartaric, citric, and acetic acids; the activity depends almost entirely on the concentration of hydrogen ions in the acid solution and the various acids thus show typical differences which correspond with their recognized degrees of dissociation. The activity of invertase is zero in alkaline solutions, rises to a maximum in very weakly acid ones, and decreases with stronger acidity

---

FEHLING'S SOLUTION.

A CONTRIBUTION TO THE HISTORY OF CHEMICAL REAGENTS.

BY B HERSTEIN.

Received March 11, 1910.

A history of chemical reagents would form no small and not the least interesting part of the history of chemistry generally, and for obvious reasons. In studying the intramolecular ous filtrate on standing. The follows strictly inductive methods, taking t of direct observation, and while for the purpothyl alcohol, chloroform compelled to classify such results into some comral recrystallizations sistent system arrived at by logical induction, such hypnd benzene. It tions are not permitted to influence the direct results of th (Kjeldahl):

Intramolecular changes of matter however are not alw observable, and to bring them into a condition where our p would be able to grasp them, we must in the majority of cases reso Di- what may be described as secondary reactions induced by foreign su stances, the so-called chemical reagents. Our processes of differentiation, upon which chemistry in general and analytical chemistry especially ultimately rest, are based upon the behavior of the various forms of matter towards different chemical reagents, and it follows from this that the progress of chemistry to a very large degree depends upon the introduction of such chemical reagents and an intimate knowledge of their working.

Thus to quote but one modern instance it is only necessary to point to the fact that the wonderful insight which we have gained within the last generation into the nature of sugars and carbohydrates generally is due almost exclusively to the introduction of phenylhydrazine as a chemical reagent. Previous to this our knowledge of this group of substances was very limited indeed, and of the few reactions characteristic for this group of substances none was better known than their behavior towards a solution of copper salts. The reaction upon which the value of this reagent in all its various modifications depends is, as is well known, based upon the reducing effect which certain sugars exert upon such solution, and although analytical chemistry has only within comparatively recent years made use of this reaction, its history runs nevertheless far back into the primitive period of human knowledge.

It undoubtedly must first have been observed by the man who introduced the so-called *unguentum Ægyptiacum* —Egyptian ointment— into materia medica, and this probably was none other than an Egyptian priest, if we may draw such conclusions from the name. This *unguentum Ægyptiacum*, which has long since disappeared from all the modern pharmacopoeias, but which for long ages was considered a very valuable medicine, forming the basis of various ointments and cosmetical preparations, was prepared by boiling together a mixture of verdigris and honey to which a few drops of vinegar were added. During the boiling the color of the mass changes considerably owing to the interaction between the glucose and the copper acetate, a change of color so striking that it could not have escaped notice. Nevertheless it has never occurred to any of these pharmacists, who in those days were the principal guardians of whatever chemistry there was, to make these changes the independent object of their studies. Quantitative attempt an explanation of the phenomena observed during able to ction was Antoine Baumé, a celebrated pharmacist of the eighteenth century, who wrote his name indelibly into the history of chemical technology by the device of his spindle. In accordance with the theory then prevailing he said in his "Traité de Pharmacie Théorique et Pratique," that in boiling honey with verdigris and vinegar it is the phlogiston of the acetic acid which, uniting with the verdigris, forms metallic copper, which is deposited. For almost one-half a century this explanation was accepted as satisfactory. During this time, however, the phlogiston theory had been entirely overthrown by Lavoisier, and a period of reconstruction had set in, which may be best described by Hegel's phrase "the re-evaluation of all values." Speculative deductions gave place to experimental research, and the balance was made the chief arbiter of the laboratory. A thorough overhauling of all chemical knowledge was undertaken, and in course of time the phenomena observed during the reaction in question were also subjected to renewed scrutiny.

In January, 1815, Dr. Vogel, of Paris, read before the French Academy of Science a paper entitled "A Research Concerning the Decomposition of Salts and Metallic Oxides by Sugars."[1] As indicated by the title, the principal object sought in this investigation was an insight into the mechanism of the reaction, while the products formed during the reaction were studied as closely as the means then permitted, both qualitatively and quantitatively, but only with a view of obtaining light upon the reaction itself. Vogel was able to show that the reddish or brown precipitate which formed on boiling copper acetate with honey and several other sugars then known was not metallic copper, but cuprous oxide, or as it was then called, copper protoxide, that the color of the precipitate depended very much on the length of time the mixture was heated, and that the precipitation is obtained only from cane, starch and grape sugar, sugar of milk, also from molasses, manna, and honey, but not from the so-called sweet principle of Scheele.[2] Vogel also observed the evolution of carbonic acid gas and acetic acid, which, however, he attributed to the high temperature to which the mixture had been subjected. Using copper sulphate instead of the acetate he claims to have precipitated metallic copper while copper chloride and copper nitrate, which were likewise tried, seemed not to be influenced at all. Similar observations made almost simultaneously with the preceding were given by J. A. Buchner, Professor of Chemistry in Munich, and published in the succeeding number of the same periodical.[3] On the whole he merely confirmed the result obtained by Vogel with this exception, that ous filtrate on standing. The red precipitate to consist of cuprous oxide, Bu the reaction the sugar is split up and that one of thyl alcohol, chloroform combines with the copper to form the precipitate. ral recrystallizations

---

[1] *Abstracted in Schweigger's Journal*, 1815, Vol. XIII, page 162.

[2] By this name glycerol, discovered in 1779 by Scheele, was known until well up into the first part of the 19th century.

[3] *Schweigger's Journal*, 1815, Vol. XIV, p. 224.

From time to time other chemists were attracted by the nd benzene. It Their work, however, did not materially broaden the problem (Kjeldahl): mained one more of theoretical than practical value until the y when Trommer published his paper, "The Differentiation between Dex Di- Cane and Grape Sugar."[2] Here the subject was approached from an entirely different and more practical point of view. Trommer was able to show that in making the copper salt solution alkaline, it became a valuable reagent for the differentiation between the various sugars and sugar giving substances. He used an alkaline solution of copper sulphate, and showed that such a solution will yet give a distinctive precipitate of cuprous oxide when boiled with solutions of grape sugar containing only one part in one hundred thousand, and that when the solution of the grape sugar is ten times more dilute, *i. e.*, containing one part to one million, the reaction is yet noticeable in reflected light. The fact that the reaction takes place only in the presence of certain sugars such as glucose, for instance, while cane sugar or dextrin are not acted upon, was fully noticed and made the basis of the differentiation between the different sugars. To Trommer thus belongs the credit of having first introduced the alkaline copper sulphate solution into analytical chemistry, though it was at first used only for qualitative purposes. But the next step was not long in coming, and within a very short time the very same reagent was recommended for use in quantitative chemical analysis.

The estimation of sugars in those days was far from being satisfactory to the chemist engaged in this line of work, depending entirely on two methods. First, the fermentation process devised by Lavoisier and others, and second, the process introduced by Biot, which was based on the deflection of polarized light by sugar solutions. Both methods have their disadvantages, the first requiring considerable time for its completion, quite aside from the fact that the decomposition into alcohol and carbonic acid gas is by no means quantitative, by-products being formed which interfere with the accuracy of the results. The polariscope gives quick and fairly accurate results; requires however clear and colorless solutions containing no foreign substances which would deflect the polarized ray. The necessity for an improved method of estimating sugars became so imperious that in 1838 a prize of 3000 francs was offered by the "Société d'encouragement pour l'industrie nationale" to the chemist who would devise a successful

---

[1] Buchholtz, Peschier, Busch, see *Annalen der Chem. und Pharm.*, 1832, Vol. IV, p. 57.

[2] *Annalen der Chem. und Pharm.*, 1841, Vol. XXXIX, page 360.

their studies. quantitative estimation of sugar. Of the answers received observed during able to the committee, and the offer was renewed from macist of the eigil in 1844 Ch. Barreswil submitted his solution.[1] The history of chemicommittee, the well-known Peligot, did not consider the with the theory satisfactory, but he nevertheless recommended that Théorique the prize, *viz.*, 1000 francs, be awarded to Barreswil for his it is the which, in his opinion,[1] though limited in its application, nevermes offered a valuable improvement on the existing methods. Barthwil's proposal consisted merely in the extension of the method suggested by Trommer for qualitative differentiation to the quantitative estimation of sugars. The main principle of Trommer's suggestion, *i. e.*, the use of the alkaline copper sulphate solution, was maintained, and the improvement introduced consisted in the addition of a solution of potassium tartrate to prevent the decomposition of the solution on heating. As proposed by Barreswil, the method was a volumetric one, the copper solution being standardized against a pure grape sugar solution of known strength, which latter was added drop by drop to the boiling copper solution, the end point of the reaction being reached when the blue color of the solution had disappeared. He also points to the necessity of inverting the cane sugar to glucose, and making two determinations, before and after inversion, where mixtures of the sugars are to be analyzed.

The principle of the method was thus established, and its practicability depended very largely upon the stability of the copper solution, which was not very satisfactory. The further efforts of the chemists who studied the subject were therefore directed mainly in this direction, although the use of the method was fully recognized and extended, as by H. Schwartz,[2] who in 1849 proposed it for the estimation of starch, which had previously to be hydrolyzed by dilute sulphuric acid to glucose. H. Fehling, by whose name the method is apparently destined to remain known in chemistry, published his first paper concerning the subject in 1848 in a medical publication, and only in 1849 he gave a more detailed account of his work to the chemical fraternity.[3] Fehling's merit consisted chiefly in having worked out with great care the details of the method, giving some account of the stoichiometrical equivalents, but neither did his solution keep for any length of time, nor did he, any more than his predecessors, recognize the fact that the reaction is quantitative only within very narrow restrictions as to the concentration of the solutions and the time of reaction. This point has been established only by the concerted efforts of the many chemists, who worked on the subject after Fehling, the necessity for keeping the copper solution divided into two parts being soon recognized. Soxhlet especially devoted much of his time to the study of the method and established[1] the exact conditions under which the determination must be carried out in order to get satisfactory results.

---

[1] Reported in *Journal de Pharmacie*, [3] 6, 301 (1844).

[2] *Ann.*, 70, 54 (1849).

[3] *Ibid.*, 72, 106 (1849); 106, 75 (1858).

BUREAU OF CHEMISTRY, WASHINGTON, D. C.

A REVIEW OF SOME RECENT INVESTIGATIONS IN THE QUINAZOLINE GROUP.[2]

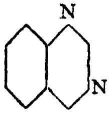
BY MARSTON TAYLOR BOGERT.

Received March 31, 1910

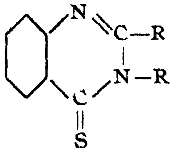
For several years past, the Organic Laboratory of Columbia University has been engaged in the synthesis and study of compounds belonging to that group of organic heterocycles known as quinazolines or phenmiazines.

To us, the work has been most interesting and enjoyable. The compounds obtained have been generally crystalline solids, quite readily purified, stable, and very satisfactory to work with.

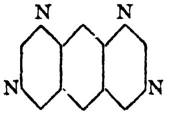
Our investigations have included—A. Quinazolines, B. Thioquinazolines, and C. Naphthotetrazines of quinazoline structure:



(Quinazoline)



(Thioquinazoline)



(1,3,7,9-Naphthotetrazine)

Incidentally, a great many new preparatory, intermediate and subsidiary products have been obtained. From the standpoint of new substances, the field has been an unusually fruitful one

It is, therefore, not only an honor but also a pleasure to present on this occasion a brief synopsis of the major lines of the work to date.

A. Quinazolines.

Colby and Dodge,[3] as the result of their investigations of the interaction of nitriles and organic acids, under conditions of heat and pressure, came to the following conclusions:

I. Fatty nitriles and aromatic acids give fatty acids and aromatic nitriles.

II. Aromatic nitriles and fatty acids give mixed secondary amides.

III. Aromatic nitriles and aromatic acids give secondary amides, unless the temperature is very high, when the nitrile of the higher radical may form.

Mathews,[4] in continuation of this work, heated acetonitrile and anthranilic acid together under pressure, hoping thereby to obtain the anthranilic nitrile. On examining the contents of the tube, he found not the nitrile desired but a colorless crystalline compound, melting at 232° (uncor.), which was not identified at the time.

---

[1] *Z. anal. Chem.*, 18; 20, 425. For other references to modern investigators see standard text-books.

[2] Address at the Twentieth Anniversary Celebration of Clark University, Worcester, Mass., Sept. 14, 1909.

[3] *Am. Chem. J.*, 13, 1 (1891).

[4] THIS JOURNAL, 20, 654 (1898).

Later, Bogert and Gotthelf[1] made a more careful study of this reaction and found that the crystalline substance melting at 232° was identical with the 2-methyl-4-ketodihydroquinazoline first described by Weddige,[2] and later obtained by Bischler and Burkart,[3] Bischler and Lang,[4] and Niementowskii.[5] By varying the nitrile, they obtained other quinazolines of analogous structure.

Continuing this work, Gotthelf[6] heated anthranilic acid under pressure with a:

IV. Fatty nitrile alone (using aceto-, propio-, *n*-butyro-, *i*-valero- and *i*-capronitriles).

V. Fatty nitrile and the corresponding fatty acid (acetonitrile and acetic acid, propionitrile and propionic acid, etc.).

VI Fatty nitrile and a higher fatty acid (acetonitrile and propionic acid, *n*-butyronitrile and capric acid, etc.).

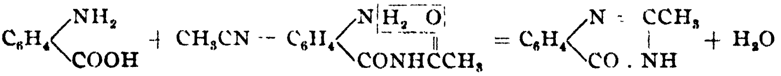
VII. Fatty nitrile and a lower fatty acid (isocapronitrile and propionic acid, etc.).

VIII. Fatty nitrile and the corresponding acid anhydride (propionitrile and propionic anhydride, valeronitrile and valeric anhydride, etc.).

IX. Fatty nitrile and higher acid anhydride (acetonitrile and propionic anhydride, etc.).

X. Fatty nitrile and lower acid anhydride (acetonitrile and formic acid, etc.).

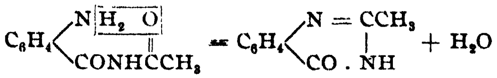
In considering case IV, Bogert and Gotthelf at the time thought it probable that the production of a quinazoline was due to the formation of an intermediate secondary amide,



$$C_6H_4\Big\langle\begin{matrix}NH_2\\COOH\end{matrix} + CH_3CN = C_6H_4\Big\langle\begin{matrix}N\boxed{H_2\ \ O}\\CONH\overset{\|}{C}CH_3\end{matrix} = C_6H_4\Big\langle\begin{matrix}N = CCH_3\\ \ \ \ \ \ \ \ |\\CO\ .\ NH\end{matrix} + H_2O$$

just as acetonitrile and acetic acid when heated under pressure give diacetoamide.[7]

One objection to this explanation of the course of the reaction lies in the fact that it involves a lactam condensation, whereas Weddige's investigations in this very field have made it quite clear that these condensations follow preferably the lactim course. If the intermediate secondary amide assumed by us passes directly into the quinazoline by loss of water, two different quinazolines should result according to whether the condensation is of lactam or lactim type:



$$C_6H_4\Big\langle\begin{matrix}N\boxed{H_2\ \ O}\\CONH\overset{\|}{C}CH_3\end{matrix} = C_6H_4\Big\langle\begin{matrix}N = CCH_3\\ \ \ \ \ \ \ \ |\\CO\ .\ NH\end{matrix} + H_2O$$

(*a*)

---

[1] THIS JOURNAL, 22, 129 (1900).

[2] *J. prakt. Chem.*, [2] 31, 124 (1885).

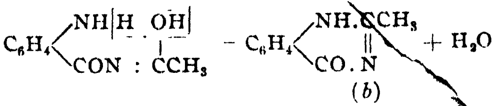
[3] *Ber.*, 26, 1350 (1893).

[4] *Ibid.*, 28, 282 (1895).

[5] *J. prakt. Chem.*, [2] 51, 564 (1895) and *Ber.*, 29, 1360 (1896).

[6] THIS JOURNAL, 23, 611 (1901).

[7] Kekulé, *Lehrbuch* (1st ed.), 1, 574; Gautier, *Ztschr. Chem.*, 1869, 127.



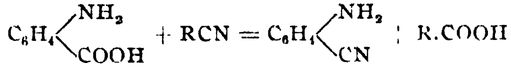
$$C_6H_4\left\langle\begin{array}{l}NH|H\ \ OH|\\ CON : CCH_3\end{array}\right. = C_6H_4\left\langle\begin{array}{l}NH.CCH_3\\ CO.N\end{array}\right. + H_2O$$

(b)

As a matter of fact, the product obtained by us is identical with (a).

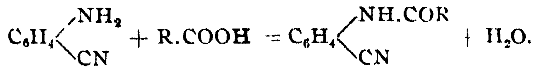
Another objection is that it is not in harmony with the conclusions of Colby and Dodge[1] cited above. According to their experiments, the first products of the action of a fatty nitrile upon an aromatic acid at high temperature and pressure are the aromatic nitrile and the fatty acid, which may and often do subsequently combine to a mixed secondary amide. That the secondary amide is not the first product seems established by their results, for in no case where a fatty nitrile acted upon an aromatic acid was the secondary amide found unaccompanied by aromatic nitrile, while in many cases aromatic nitrile and fatty acids were found unaccompanied by any secondary amide. Thus, acetonitrile and benzoic acid at 220° gave no acetobenzamide, but only benzonitrile and acetic acid, whereas when the latter two were heated together at 220°, only acetobenzamide was formed.

It therefore seems probable that the first phase of the reaction between anthranilic acid and a fatty nitrile is as follows



$$C_6H_4\left\langle\begin{array}{l}NH_2\\ COOH\end{array}\right. + RCN = C_6H_4\left\langle\begin{array}{l}NH_2\\ CN\end{array}\right. + R.COOH$$

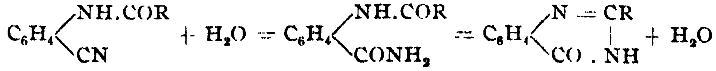
As aniline when heated to sufficiently high temperatures with fatty acids yields the corresponding anilides,[2] the second phase of the reaction is probably



$$C_6H_4\left\langle\begin{array}{l}NH_2\\ CN\end{array}\right. + R.COOH = C_6H_4\left\langle\begin{array}{l}NH.COR\\ CN\end{array}\right. + H_2O.$$

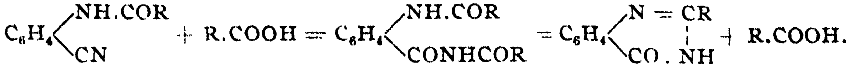
As the ease with which this acylation takes place decreases with increase in the molecular weight of the fatty acid, the higher nitriles should give smaller yields of the quinazoline, and this was found to be the case. The yield with propionitrile, for example, was 22 5 per cent., while with valeronitrile it was only 5 per cent. of the theoretical.

The acylanthranilic nitrile may then pass into the quinazoline by either of the following reactions:



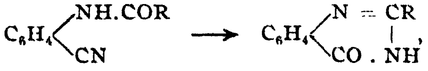
$$C_6H_4\left\langle\begin{array}{l}NH.COR\\ CN\end{array}\right. + H_2O = C_6H_4\left\langle\begin{array}{l}NH.COR\\ CONH_2\end{array}\right. = C_6H_4\left\langle\begin{array}{l}N = CR\\ |\\ CO.NH\end{array}\right. + H_2O$$

or



$$C_6H_4\left\langle\begin{array}{l}NH.COR\\ CN\end{array}\right. + R.COOH = C_6H_4\left\langle\begin{array}{l}NH.COR\\ CONHCOR\end{array}\right. = C_6H_4\left\langle\begin{array}{l}N = CR\\ |\\ CO.NH\end{array}\right. + R.COOH.$$

That a simple molecular rearrangement of the acylanthranilic nitrile occurs,



$$C_6H_4\left\langle\begin{array}{l}NH.COR\\ CN\end{array}\right. \longrightarrow C_6H_4\left\langle\begin{array}{l}N = CR\\ |\\ CO.NH\end{array}\right.,$$

seems unlikely, for the reason that when acetoanthranilic nitrile was heated for some time above its melting point, or when its solution in dry toluene was heated to high temperatures in sealed tubes, no change whatever occurred.[1] Moisture was, of course, rigidly excluded in these experiments, since a small amount of water, by successive addition and splitting off, would suffice to convert an indefinite amount of the nitrile to the quinazoline.

---

[1] *Loc. cit.*

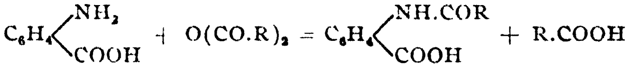
[2] Williams, *Ann.*, 131, 288; Pebal, *Ibid.*, 91, 152.

In further support of the assumption that the acylanthranilic nitrile is an intermediate product, are the following facts: (1) Acetanilide is found as a by-product in the tubes.[2] (2) The presence of a small amount of acetic anhydride greatly increases the yield of quinazoline. (3) The same quinazoline results when acetoanthranilic acid is heated in a sealed tube with acetonitrile as when anthranilic acid itself is used.[3] (4) Acetoanthranilic nitrile on partial hydrolysis changes immediately to the quinazoline.[4]

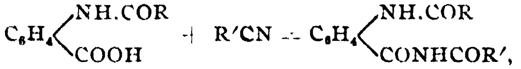
The by-products observed in the experiments were carbon dioxide, aniline, anilides, amides and ammonia. Of these, carbon dioxide and aniline are normal decomposition products of anthranilic acid at high temperatures. Partial hydrolysis of the nitrile accounts for the presence of amide. Aniline acting on the latter,[5] or upon the fatty acid present, yields the anilide, the by-product in the former case being ammonia.

In those cases (V, VI and VII) where the anthranilic acid was heated with both the fatty nitrile and the fatty acid, the results are confusing and the interpretation obscure. Quinazolines were formed, but the course of the reactions is not clear and additional work is needed before any satisfactory conclusions can be reached.

When an acid anhydride was added to the tubes containing the anthranilic acid and fatty nitrile (VIII, IX and X), the anhydride used determined the quinazoline formed in practically every case. In these experiments, the reaction is therefore probably as follows:

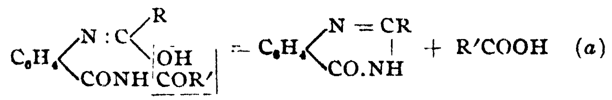


$$C_6H_4{<}\begin{array}{l}NH_2\\ COOH\end{array} + O(CO.R)_2 = C_6H_4{<}\begin{array}{l}NH.COR\\ COOH\end{array} + R.COOH$$

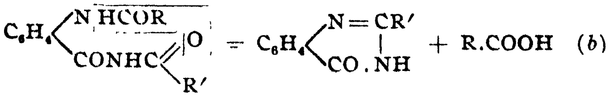


$$C_6H_4{<}\begin{array}{l}NH.COR\\ COOH\end{array} + R'CN = C_6H_4{<}\begin{array}{l}NH.COR\\ CONHCOR',\end{array}$$

the latter then condensing in either of the following ways:



$$C_6H_4{<}\begin{array}{l}N:C{<}\begin{array}{l}R\\ OH\end{array}\\ CONH\,COR'\end{array} = C_6H_4{<}\begin{array}{l}N = CR\\ \quad\;\;\vert\\ CO.NH\end{array} + R'COOH \quad (a)$$



$$C_6H_4{<}\begin{array}{l}N\,HCOR\\ CONHC{\ll}\begin{array}{l}O\\ R'\end{array}\end{array} = C_6H_4{<}\begin{array}{l}N = CR'\\ \quad\;\;\vert\\ CO.NH\end{array} + R.COOH \quad (b)$$

The nitrile was used with the corresponding acid anhydride (VIII), with a higher acid anhydride (IX), and with a lower anhydride (X). Of these, types VIII and IX invariably yielded pure quinazolines according to reaction (*a*) above. Only when a lower anhydride was used with the nitrile (X), were products encountered which were mixtures of quinazolines.

---

[1] Bogert and Hand, This Journal, 24, 1034 (1902).

[2] Bogert and Gotthelf, *Ibid.*, 22, 528 (1900).

[3] Bogert and Gotthelf, *Loc. cit.*

[4] Bogert and Hand, *Loc. cit.*

[5] Kelbe, *Ber.*, 16, 1200 (1883).

Of these different sealed-tube reactions, much the best was that in which the anthranilic acid was heated with the fatty nitrile and the corresponding acid anhydride (VIII). The yield by this process was fair (30 to 50 per cent. of the theory) and, unless the heating was too high, the tube contents were invariably light-colored and crystalline.

In the foregoing, it is assumed that the secondary amide is an intermediate product in the formation of the quinazoline. Such an amide, R.CO.NH.CO.R′, being symmetrical, should be producible either from R.COOH and R′CN, or from R′COOH and RCN. In other words, since the formation of the —CO.NH.CO— group is due solely to the combination of the CN and COOH, it should make no difference which radical carries the CN and which the COOH. The same secondary amide and, therefore, the same quinazoline, should result whether the acylanthranilic acid is heated with the fatty nitrile, or the acylanthranilic nitrile with the fatty acid (or its anhydride). On testing this practically,[1] such was indeed found to be the case, and a number of quinazolines were thus obtained from the acylanthranilic nitriles by heating them in sealed tubes with the fatty acid or, better, its anhydride.

In experimenting with these acylanthranilic nitriles, a method of converting them into the quinazolines, far superior to any of the methods described above, was discovered. It consists in digesting the acylanthranilic nitrile for a few minutes with a warm alkaline dioxide solution, and is really a beautiful method, being very rapid, simplicity itself in execution, and giving large yields of practically pure quinazolines. It depends upon the hydrolysis of the nitrile to the amide, the acylanthranilamide then condensing to the quinazoline, as shown by Weddige.[2]

In those cases where the *o*-amino acid is best obtained from its nitrile by saponification, it is convenient to be able to pass direct from the nitrile to the quinazoline. Thus, homoanthranilic nitrile is readily prepared from *m*-nitro-*p*-toluidine, through *m*-nitro-*p*-toluonitrile, and from the acyl derivatives of this homoanthranilic nitrile and an alkaline dioxide solution (hydrogen dioxide solution made alkaline with sodium hydroxide), the 7-methyl-4-quinazolones were prepared.[3]

By a number of different processes, including those already mentioned, starting with brominated anthranilic acids, bromoquinazolines were prepared.[4]

Our attention was next turned to the nitroquinazolines, and many were made from nitroanthranilic acids by the methods already described, and also by heating the ammonium salt of the nitroanthranilic acid with formamide,[5] by the direct action of heat on the ammonium salts of nitroacylanthranilic acids,[6] and by the action of primary amines on nitroacetoanthranils.[7] The last is a very fine method indeed, and one we have developed quite extensively.

[1] Bogert and Hand, This Journal, 24, 1031 (1902).

[2] *J. prakt. Chem.*, [2] 31, 124 (1885); 36, 141 (1887).

[3] Bogert and Hoffman, This Journal, 27, 1293 (1905).

[4] Bogert and Hand, *Ibid.*, 25, 943 (1903); 28, 94 (1906).

[5] Niementovskii, *J. prakt. Chem.*, [2] 51, 564 (1895).

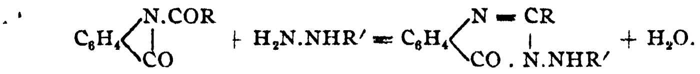
[6] Bischler and Burkart, *Ber.*, 26, 1349 (1893).

[7] Anschütz, Schmidt and Greiffenberg, *Ber.*, 35, 3480 (1902).

By these various methods, we prepared 5-nitro-,[1] 6-nitro-,[2] and 7-nitro-4-quinazolones.[3] Of the four possible types of benzoylnitroquinazolines, representatives of the 6-nitro,[4] and 8-nitro,[5] were already known. The preparation of the 5- and 7-nitro derivatives completed the series.

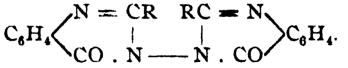
Reduction of the nitroquinazolines yielded the corresponding benzoylaminoquinazolines,[6] in which, as might have been expected, the amino group shows the usual aniline reactions.

Aminoquinazolines with the amino group on the miazine side of the nucleus were produced by condensing simple or substituted acylanthranils with primary hydrazines,[7]



$$C_6H_4\left\langle\begin{array}{l}N.COR\\ |\\ CO\end{array}\right. + H_2N.NHR' = C_6H_4\left\langle\begin{array}{l}N = CR\\ \qquad |\\ CO\,.\,N.NHR'\end{array}\right. + H_2O.$$

With hydrazine itself, it was also found possible to condense two molecules of the anthranil with one of the hydrazine, thereby giving 3,3′-diquinazolonyls,



$$C_6H_4\left\langle\begin{array}{l}N = CR \quad RC = N\\ \qquad | \qquad\quad |\\ CO\,.\,N \text{———} N\,.\,CO\end{array}\right\rangle C_6H_4.$$

The same result can be accomplished, though less satisfactorily, by condensing the 3-aminoquinazoline with a second molecule of the anthranil. The di-quinazolonyls so far isolated are all very difficultly soluble and inert.

The 3-aminoquinazolines proved interesting because of their unsymmetrical secondary hydrazine structure, $>N.NH_2$. In the main, their properties coincide with those of other N-amino heterocyclic compounds. Thus, nitrous acid does not diazotize the amino group, but replaces it by hydrogen; with diacetosuccinic esters, they often yield pyrrole derivatives;[8] with aromatic nitroso bodies, they do not give azo compounds; nor are they oxidized to tetrazones by mercuric oxide. On the other hand, they do not usually condense with ketones, while they do occasionally yield phenyluramino derivatives with phenyl isocyanate.[9] In the elimination of the N-amino group by the action of nitrous acid, there must be some unstable intermediate product formed, for if immediately after the addition of the nitrous acid the mixture be poured into an alkaline solution of alpha- or beta- naphthol, dyestuffs are formed of considerable tinctorial power, the structure of which has not been elucidated.

Further experimentation with the acylanthranils showed that they could also be condensed with amino nitriles or amino esters to the corresponding quinazolines.[1]

---

[1] Bogert and Chambers, THIS JOURNAL, 27, 649 (1905); Bogert and Seil, *Ibid.*, 27, 1305 (1905) and 29, 532 (1907).

[2] Bogert and Cooke, *Ibid.*, 28, 1449 (1906).

[3] Bogert and Steiner, *Ibid.*, 27, 1327 (1905); Bogert and Seil, *Ibid.*, 29, 532 (1907); Bogert and Klaber, *Ibid.*, 30, 807 (1908).

[4] Dehoff, *J. prakt. Chem.*, [2] 42, 347 (1890); Thieme, *Ibid.*, 43, 441 (1891).

[5] Zacharias, *Ibid.*, 43, 441 (1891).

[6] Bogert and Chambers, THIS JOURNAL, 28, 207 (1906); Bogert and Klaber, *Ibid.*, 30, 807 (1908).

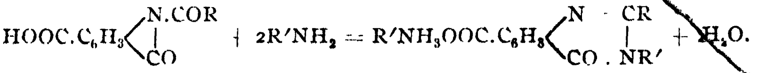
[7] Bogert and Seil, *Ibid.*, 28, 884 (1906); Bogert and Cook, *Loc. cit.*; Bogert and Klaber, *Loc. cit.*

[8] Bülow, *Ber.*, 35, 4312 (1902); 39, 2621 and 3372 (1906).

[9] Bogert and Gortner, THIS JOURNAL, 31, 943 (1909).

The ease with which acylanthranils condense with primary amines to crystalline quinazolines suggests the utilization of this reaction for the separation and identification of easily soluble or sirupy amines difficult to handle otherwise.

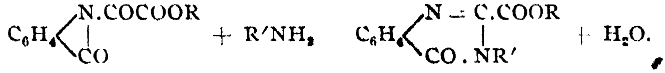
The same reaction was employed for the preparation of quinazoline carboxylic acids from acylanthranil carboxylic acids,[2]



$$HOOC.C_6H_3\left\langle\begin{matrix}N.COR\\|\\CO\end{matrix}\right. + 2R'NH_2 = R'NH_3OOC.C_6H_3\left\langle\begin{matrix}N - CR\\|\\CO.NR'\end{matrix}\right. + H_2O.$$

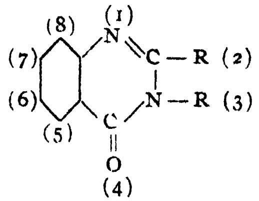
These quinazoline benzoylcarboxylic acids are colorless crystalline solids, melting with decomposition above 300°, more or less soluble in alcohol, but very difficultly soluble in other neutral organic solvents.

From the oxalyl anthranils, quinazolinecarboxylic acids were prepared carrying the carboxyl group on the miazine side of the nucleus,[3]

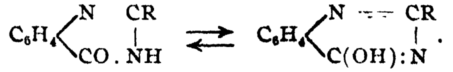


$$C_6H_4\left\langle\begin{matrix}N.COCOOR\\|\\CO\end{matrix}\right. + R'NH_2 \quad C_6H_4\left\langle\begin{matrix}N = C.COOR\\|\\CO.NR'\end{matrix}\right. + H_2O.$$

The particular quinazolines described in the foregoing are for the most part of the type designated as 4-ketodihydroquinazolines or, more simply, 4-quinazolones,



When there is an H at position 3 instead of a radical, there arises the possibility of keto-enolic tautomerism,



$$C_6H_4\left\langle\begin{matrix}N \quad CR\\|\\CO.NH\end{matrix}\right. \rightleftarrows C_6H_4\left\langle\begin{matrix}N == CR\\|\\C(OH):N\end{matrix}\right. .$$

(4-Quinazolone) (4-Hydroxyquinazoline)

All those 4-quinazolones (4-hydroxyquinazolines) which carry a hydrogen at position 3 are easily soluble in aqueous solutions of the caustic alkalies and re-precipitable from such solutions by carbon dioxide or acetic acid. When these alkali salts are treated with alkyl halides, the 3-(*N*)alkyl derivative is the chief product.[4] The nitro derivatives furnish an apparent exception to this, in that the product with the higher alkyl halides is reported as chiefly the oxygen ether (*i. e.*, the 4-(*O*)alkyl, or -OR compound).[5] We are somewhat skeptical, however, of the accuracy of these results and feel that they should not be fully accepted until the pure oxygen ethers have been prepared by other processes and the two products compared. One reason for this skepticism on our part is that certain of these supposititious oxygen ethers could not be hydrolyzed with concentrated mineral acids (hydrochloric), a result contrary to our experience and to that of others working with true oxygen ethers.

---

[1] Bogert and Kláber, *Loc. cit.*

[2] Bogert, Wiggin and Sinclair, THIS JOURNAL, 29, 82 (1907); Bogert and Jouard, *Ibid.*, 31,489 (1909).

[3] Bogert and Gortner, *Ibid.*, 32, 119 (1910).

[4] Bogert and May, *Ibid.*, 31, 507 (1909).

[5] Bogert and Seil, *Ibid.*, 29, 517 (1907).

Pure 3-(*N*)alkyl derivatives are easily obtained by the acylanthranil reaction already described. For the isomeric 4-OR derivatives, the best method appears to be the treatment of the 4-chloroquinazolines with sodium alcoholates.[1] In the case of the simple alkyl derivatives of unsubstituted 4-quinazolones (4-hydroxyquinazolines), the (3)-NR compounds are colorless, odorless solids, quite soluble in water, generally very difficultly volatile with steam, of higher melting point than the 4-OR isomers, and are not hydrolyzed by strong hydrochloric acid. On the other hand, the 4-OR compounds are oily liquids or low-melting solids, usually of pleasant odor, readily volatile with steam, less soluble in water but more soluble in hydrochloric acid than the NR isomers, and are readily hydrolyzed by mineral acids to the hydroxyquinazoline (4-quinazolone) again. Some of the lower ones can even be distilled undecomposed at ordinary pressure.

In the preparation of the 4-chloroquinazolines from the 4-hydroxyquinazolines (4-quinazolones),[1] a methyl or ethyl group in position 2 exerts a peculiar influence upon the course of the reaction with phosphorus halides or similar halogenating reagents. In all such cases, it was found impossible to replace the OH at 4 by chlorine without simultaneously introducing three chlorine atoms in the benzene part of the nucleus. Even when 2,3-dimethyl-4-quinazolone was heated with phosphorus penta- and oxychlorides,[2] the 3-methyl group was split off, a Cl attached itself at 4, but again three Cl's entered the benzene nucleus.

Our investigations in this 4-quinazolone group have led to the synthesis and study of derivatives carrying the following substitutions:

1. At position, 2-,methyl, ethyl, normal and isopropyl, isobutyl, isoamyl, phenyl, *m*- and *p*-nitrophenyl, benzyl, *p*-tolyl, COOH, and various complex radicals and residues.
2. At position, 3-,methyl, ethyl, normal and isopropyl, iso- and secondary butyl, isoamyl, allyl, phenyl, *o*-tolyl, *p*-anisyl, benzyl, beta-naphthyl, CH_2COOR, CH_2CONH_2, CH_2CN, C_6H_4COOR, $C_6H_4CONH_2$, C_6H_4CN, the amino group and its derivatives, quinazolonyls, and dimethyl dicarbethoxypyrrole.
3. At position, 4-,OH, Cl, and OR.
4. On the benzene nucleus-,alkyls, halogens, nitro, amino (and derivatives), and COOH.

In the various series, where homologs of analogous structure are compared, it will be found that the melting point falls quite steadily with rise in molecular weight, the iso compounds melting higher than the isomers carrying normal alkyls. This is perhaps not so surprising since many series of anthranilic compounds (for example, the alkyl and acylamino anthranilic acids, the acylanthranilic nitriles, etc.) exhibit a similar behavior.

In addition to the 4-quinazolones, our studies have included also the 2-quinazolones (2-hydroxyquinazolines), 2,4-dihydroxyquinazolines (2,4-

---

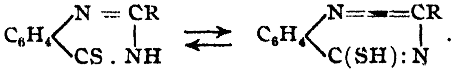
[1] Bogert and May, *Loc. cit.*

[2] Compare Fischer, *Ber.*, 32, 1297 (1899).

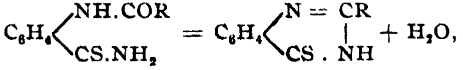
diketotetrahydroquinazolines, or benzoylene ureas), and a few other types.

B. Thioquinazolines.

The work in the domain of the oxygenated quinazolines led quite naturally to the production of bodies of analogous structure carrying sulphur instead of oxygen, and known as the 4-thioquinazolone or quinazolthion (4) type,[1]

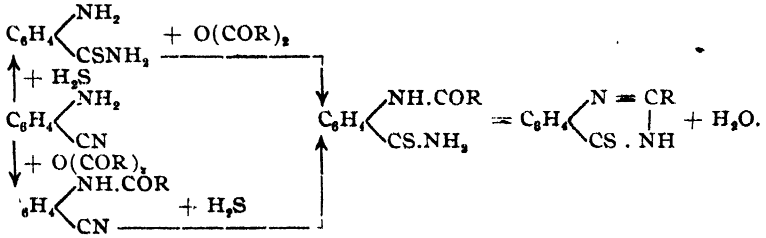


Since anthranilamides, as noted, easily condense to quinazolines by loss of water, it seemed probable that the corresponding thioamides would yield thioquinazolines,



and the results corroborated this fully.

The acylanthranilic thiamide was prepared either by first converting the anthranilic nitrile to the amide by the direct addition of hydrogen sulphide and then acylating, or by first acylating and then adding the H_2S:



By the use of thiol acids (for example, thioacetic acid) in sealed tubes, the thioquinazoline was obtained direct. The thiol acid first acylates the amino group. The by-product of this acylation, H_2S, cannot escape from the tube and is thus forced to attach itself to the CN, thereby changing it to the thioamide. The acylaminothioamide then passes to the thioquinazoline by loss of water.

As comparatively few thiol acids are readily available, we made our reaction more widely applicable by substituting the acid anhydride with sodium sulphide for the thiol acid. Thus, when anthranilic nitrile is heated with acetic anhydride and sodium sulphide in open flasks or, better, in sealed tubes, the anhydride first acetylates the amino group with formation of acetic acid as the by-product. The latter then attacks the sodium sulphide, setting free hydrogen sulphide and forming sodium acetate. The hydrogen sulphide converts the acetoanthranilic nitrile to the thioamide, which then splits out water and gives the quinazoline, the sodium acetate possibly assisting in the elimination of this molecule of water.

These thioquinazolines crystallize in beautiful yellow needles or prisms when alcohol is used as the solvent. By virtue of the $\text{—CS.NH—} \rightleftarrows \text{—C(SH) : N—}$ group, they dissolve freely in solutions of the caustic alkalies and are reprecipitated therefrom by carbon dioxide or by acetic acid.

---

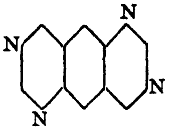
[1] Bogert, Breneman and Hand, This Journal, 25, 372 (1903); Bogert and Hand, *Ibid.*, 25, 935 (1903).

Like the corresponding oxygen compounds, the melting point of the 2-alkyl derivatives steadily falls with rise in molecular weight, the iso compounds melting higher than the isomers of normal structure.

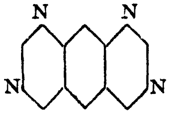
In the course of the investigation, we have used both simple and substituted anthranilic acids.

C. Naphthotetrazines.

Our syntheses of the simple quinazolines having resulted so satisfactorily, we decided to attempt the synthesis of compounds of the following types,



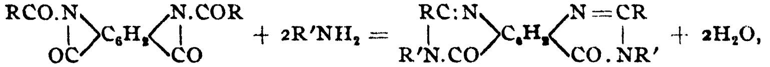
(1,3,6,8-Naphthotetrazine)



(1,3,7,9-Naphthotetrazine)

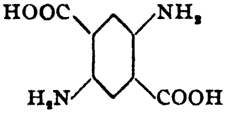
and in this were equally fortunate.

Naphthotetrazines of both types were prepared from the bis-acylanthranils of the appropriate diaminophthalic acid and various primary amines,[1]

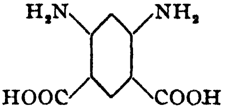


$$\begin{array}{c}RCO.N\\ |\\ OC\end{array}\!\!>C_6H_2<\!\!\begin{array}{c}N.COR\\ |\\ CO\end{array} + 2R'NH_2 = \begin{array}{c}RC:N\\ |\\ R'N.CO\end{array}\!\!>C_6H_2<\!\!\begin{array}{c}N=CR\\ |\\ CO.NR'\end{array} + 2H_2O,$$

as well as from the diaminophthalic acids themselves by reactions similar to those employed for the synthesis of the simple quinazolines. The diaminophthalic acids used, which must be, of course, of anthranilic structure, were



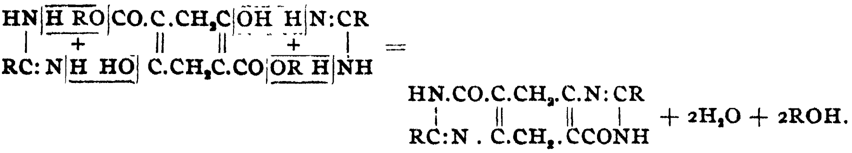
(3,6-Diamino-1,4-phthalic acid)



(4,6-Diamino-1,3-phthalic acid)

These acids, as can be seen by a glance at their graphic formulas, are only double anthranilic acids, and undergo similar reactions, the former yielding the 1,3,6,8-naphthotetrazines, and the latter the 1,3,7,9-isomers.

1,3,6,8-Naphthotetrazines were also obtained by condensing succinylosuccinic esters with amidines:[2]



$$\begin{array}{l} HN|H\ RO|CO.C.CH_2C|OH\ H|N:CR \\ |\quad + \qquad \| \qquad \| \qquad + \quad | \\ RC:N|H\ HO|\ C.CH_2C.CO|OR\ H|NH\end{array} = \begin{array}{l}HN.CO.C.CH_2.C.N:CR\\ |\qquad \| \qquad \| \qquad | \\ RC:N\ .\ C.CH_2.CCONH\end{array} + 2H_2O + 2ROH.$$

All of these naphthotetrazine derivatives so far obtained by the above processes are either infusible or melt very high. They are insoluble in the ordinary neutral organic solvents. When they carry the —NH.CO—

---

[1] Bogert and Nelson, THIS JOURNAL, 29, 729 (1907); Bogert and Kropff, *Ibid.*, 31, 1071 (1910).

[2] Bogert and Dox, *Ibid.*, 27, 1127 and 1302 (1905).

$\rightleftarrows$ —N : C(OH)— group, they dissolve readily in solutions of the caustic alkalies, whence they are reprecipitated by carbon dioxide or by acetic acid.

The naphthotetrazine prepared from guanidine and succinylosuccinic ester gives a sodium salt crystallizing in beautiful yellow needles or prisms which have a magnificent greenish fluorescence.

This, in a very hasty and imperfect way, indicates the main lines along which this particular field of investigation has been developed. It would only weary you to refer even hurriedly to the many subordinate lines of investigation radiating from these main ones, necessitating or resulting in the synthesis of many hundreds of new organic substances. I can only say, as I did at the outset of this address, that it has all been most interesting to us, and that we are still carrying on the work.

The articles published in the progress of these researches are listed below. They have all appeared in *The Journal of the American Chemical Society*, to which the volume numbers refer:

1900 1. A new synthesis in the quinazoline group. M. T. Bogert and A. H. Gotthelf, THIS JOURNAL, 22, 129.

2. The direct synthesis of ketodihydroquinazolines from orthoamino acids. M. T. Bogert and A. H. Gotthelf, *Ibid.*, 22, 522.

1901 3. The synthesis of alkyl ketodihydroquinazolines from anthranilic acid. A. H. Gotthelf, *Ibid.*, 23, 611.

1902 4. The synthesis of alkyl ketodihydroquinazolines from anthranilic nitrile. M. T. Bogert and W. F. Hand, *Ibid.*, 24, 1031.

1903 5. The synthesis of alkyl thioketodihydroquinazolines from anthranilic nitrile. M. T. Bogert, H. C. Breneman and W. F. Hand, *Ibid.*, 25, 372.

6. 3,5-Bibrom-2-aminobenzoic acid; its nitrile and the synthesis of quinazolines from the latter. M. T. Bogert and W. F. Hand, *Ibid.*, 25, 935.

1905 7. The synthesis of 5-nitro-4-ketodihydroquinazolines from 6-nitro-2-aminobenzoic acid, 6-nitro-2-acetylaminobenzoic acid, and from the corresponding nitro acetylanthranil. M. T. Bogert and V. J. Chambers, *Ibid.*, 27, 649.

8. The condensation of succinylosuccinic acid diethyl ester with guanidine. A derivative of 1,3,5,7-naphthotetrazine, a new heterocycle. M. T. Bogert and A. W. Dox, *Ibid.*, 27, 1127.

9. Some acyl derivatives of homoanthranilic nitrile, and the 7-methyl-4-ketodihydroquinazolines prepared therefrom. M. T. Bogert and A. Hoffman, *Ibid.*, 27, 1293.

10. The condensation of succinylosuccinic acid diethyl ester with acetamidine: 2,6-dimethyl-4,8-dihydroxy-9,10-dihydro-1,3,5,7-naphthotetrazine. M. T. Bogert and A. W. Dox, *Ibid.*, 27, 1302.

11. The synthesis of 2-methyl-5-nitro-4-ketodihydroquinazolines from 6-nitro acetanthranil and primary amines. M. T. Bogert and H. A. Seil, *Ibid.*, 27, 1305.

12. The synthesis of 7-nitro-2-alkyl-4-ketodihydroquinazolines from 4-nitro acetanthranilic acid and from 4-nitro acetanthranil. M. T. Bogert and S. H. Steiner, *Ibid.*, 27, 1327.

13. 5-Brom-2-aminobenzoic acid and some of its derivatives. M. T. Bogert and W. F. Hand, *Ibid.*, 27, 1476.

1906 14. The preparation of 6-brom-4-ketodihydroquinazolines from 5-brom-2-aminobenzoic acid and certain of its derivatives. M. T. Bogert and W. F. Hand, *Ibid.*, 28, 94.

15. On 5-amino-4-ketodihydroquinazolines and 5-amino-2-methyl-4-ketodihydroquinazolines. M. T. Bogert and V. J. Chambers, *Ibid.*, **28**, 207.

16. On the condensation of succinylosuccinic esters with amidines. M. T. Bogert and A. W. Dox, *Ibid.*, **28**, 398.

17. On a 3-aminoquinazoline and the corresponding 3,3′-diquinazolyl, from 6-nitro acetanthranil and hydrazine hydrate. M. T. Bogert and H. A. Seil, *Ibid.*, **28**, 884.

18. Synthesis of 6-nitro-2-methyl-4-ketodihydroquinazolines from 5-nitro acetanthranil and primary amines. M. T. Bogert and E. P. Cook, *Ibid.*, **28**, 1449.

1907 19. The synthesis of quinazoline carboxylic acids from 4-aminoisophthalic acid and from aminoterephthalic acid. M. T. Bogert, J. D. Wiggin and J. E. Sinclair, *Ibid.*, **29**, 82.

20. A strange case of poisoning. M. T. Bogert, *Ibid*, **29**, 239.

21. On 2,3-dialkyl-4-quinazolones and the products obtained by alkylating 2-alkyl-4-quinazolones (2-alkyl-4-hydroxyquinazolines). M. T. Bogert and H. A. Seil, *Ibid.*, **29**, 517.

22. The synthesis of 1,3,6,8-naphthotetrazines from paradiaminoterephthalic acid and from certain of its derivatives. M. T. Bogert and J. M. Nelson, *Ibid.*, **29**, 729

1908 23. On certain 7-nitro-2-methyl-4-quinazolones from 4-nitroacetanthranil. M. T. Bogert and W. Klaber, *Ibid*, **30**, 807.

1909 24. 3-Amino-*o*-phthalic acid and certain of its derivatives. M. T. Bogert and F. L. Jouard, *Ibid.*, **31**, 483.

25 On certain quinazoline oxygen ethers of the type —N:C(OR)— and the isomeric -NR.CO— compounds. M. T. Bogert and C. E. May, *Ibid.*, **31**, 507.

26 On some amino and nitroamino derivatives of benzoic, metatoluic and metaphthalic acids M. T. Bogert and A. H. Kropff, *Ibid.*, **31**, 841.

27. On 2-methyl-3-amino-4-quinazolone and certain of its derivatives M. T. Bogert and R. A. Gortner, *Ibid.*, **31**, 943.

28. On 6-methyl-7-aminoquinazolones, 7-nitroquinazolone-6-carboxylic acids, and 1,3,7,9-naphthotetrazines M. T. Bogert and A. H. Kropff, *Ibid.*, **31**, 1071.

1910 29. On oxalyl anthranilic compounds and quinazolines derived therefrom M. T. Bogert and R. A. Gortner, *Ibid.*, **32**, 119.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
March 28, 1910

THE CAUSE OF COLOR IN ORGANIC COMPOUNDS.[1]

BY RICHARD SYDNEY CURTISS

Received April 16, 1910.

During an investigation in the mesoxalic ester series, I have been led to a study of the causes which underlie the phenomenon of color in some of these very simple aliphatic compounds.[2] In doing so I have found the subject fascinating, and it has seemed to me that it might be of interest to a general audience, in which I assume the great majority are not organic chemists. I shall try to present some of the simpler facts and theories on which our ideas of color cause rest.

---

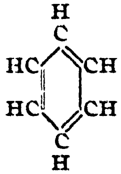
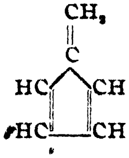
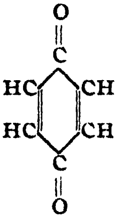
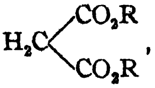
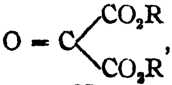
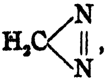
[1] Address of the Chairman of the Division of Organic Chemistry of the American Chemical Society delivered in general session of the Society at Harvard University, December 29, 1909.

[2] Curtiss and Spencer, THIS JOURNAL, **31**, 1033; Curtiss, *Am. Chem. J.*, **35**, 477.

To discuss a subject in an hour, upon which so many thousands of pages of interesting researches have appeared, would be difficult enough, but my task is the harder since our good secretary has limited us to thirty minutes.

In deference to my non-organic friends, I shall try to eliminate, as far as possible, those incomprehensibly long names and formulas, which, while so simple and luminous to us, are always thorns in the flesh to most young chemists.

By a colored substance we all understand one which has the power of retaining or holding back some of the ether vibrations of certain definite wave length of the white light falling on it, the color being the resultant effect of all waves which pass through the substance to the eye. In other words, the color seen is the complement of the color absorbed.

It might be asked, Why is one compound colored and another not? Why is benzene, , colorless while its isomer, fulvene,[1] , like its oxygen derivative quinone, , is yellow? Or again, why is malonic ester,  $H_2C(CO_2R)_2$, without color and oxomalonic ester,  $O = C(CO_2R)_2$, green, formaldehyde, $H_2C = O$, colorless, and diazo methane,  $H_2C\langle N{=}N\rangle$, yellow? These are simple cases of color. They all contain an *unsaturated* group of atoms—the ethylene, the carbonyl, the azo groups.

Graebe and Liebermann,[2] who made the first studies of the relation of color to structure, noticed in 1867 that reduction of these unsaturated groups destroyed the color instantly. In the sixties little was known about the constitution of any of the organic colored substances—though, alizarin, purpurin, fuchsin, indigo and others were being investigated. Quinone was the only one whose constitution was known. It was the study of compounds like quinone and azobenzene containing such groups, and their loss of color on reduction, that led Witt[3] to formulate in 1876 his celebrated "chromophore theory." This states that the color in an organic compound is caused by the presence of a certain group which he called a *chromophore*, or color-forming group.

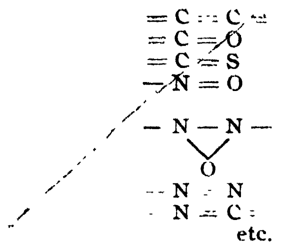
---

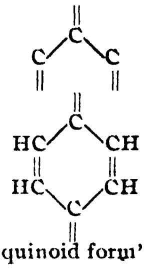
[1] J. Thiele, *Ber.*, 33, 667; *Ann.*, 348, 12.

[2] *Ber.*, 1, 106.

[3] *Ibid.*, 9, 522–524.

Chromophores.



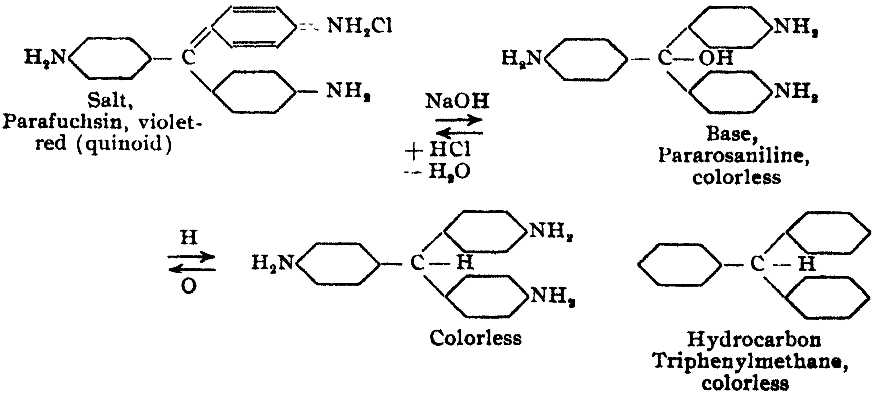


"quinoid form"
Color lost by reduction

Such a colored substance he called a *chromogen*. He also noticed that a colored substance might lack the power of imparting its color to a fabric, and that the presence of an hydroxyl or amine group, both salt-forming groups, usually tended to deepen the color and to cause it to fix to the fiber, that is, to produce a dye. Such groups he called *auxochromes*—and stated that both chromophore and auxochrome groups must be present to produce a *dye*. Witt's color theory has been of great value as a guide in the synthesis of a multitude of colored substances and dyes.

One feature that Graebe and Liebermann, in 1868, considered of fundamental importance for color production was the presence in aromatic chromogens of a quinone group or a quinone-like union of atoms, called also "quinoid form," and it is remarkable that this idea, based as it was at that time on wholly insufficient data, has been, and is even to-day in a modified form, one of the most valuable concepts in our theories of the cause of color.

In 1878–9 the cousins Emil and Otto Fischer,[1] in a series of masterly researches, established the relation of the important dyes, fuchsin and related compounds, to the parent hydrocarbon triphenylmethane and ascribed to parafuchsin a paraquinone structure, though they gave it the peroxide form. The chart shows the simple relation and color changes of this important class of dyes.



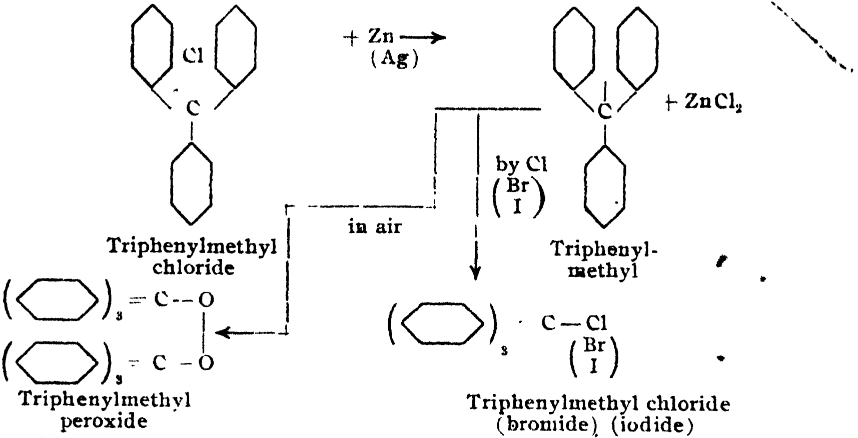
---

[1] *Ber.*, 12, 2344.

Such a molecular rearrangement as is shown in this salt formation, accompanied by an intensification of color, we shall note as a very important fact in the study of the causes of color.

The structure of these important dyes being thus settled as quinoid compounds, the color question of triphenylmethane derivatives remained quiescent for twenty years.

In 1900, Professor Gomberg[1] discovered triphenylmethyl, a colorless, crystalline product of the action of zinc on triphenylmethyl chloride in dry benzene, air being excluded during the reaction.



Its behavior is very remarkable. It unites with oxygen of the air to form a peroxide. Chlorine produces triphenylmethyl chloride. Its chloride forms with metallic chlorides colored addition products; with acids it gives colored salts. It even adds neutral substances like benzene and ether. Its great reactivity and apparently unsaturated character led Gomberg to believe that at last the object was attained for which Frankland had sought in vain in the early days of organic chemistry, the preparation of a free methyl radical. In the meantime the trivalency of carbon received an apparent set back when it was discovered that Gomberg's triphenylmethyl had a molecular weight corresponding to hexaphenylethane, $(C_6H_5)_3C{-}C(C_6H_5)_3$. The reactivity and unsaturated nature of this new substance cannot, however, be explained by this formula.

As a result of studies on this substance by Ullmann and Borsum,[2] Heintschel,[3] Chichibabin,[4] Schmidlin, Jacobson,[5] Gomberg,[6] Gomberg and Cone[7] and others, a formula was proposed by Jacobson, which well explains its properties, *when in solution.* This formula (below) shows it as a derivative of quinol. In quinol the CH_3 group easily dissociates, or wanders, to another part of the molecule.

---

[1] This Journal, 22, 757; *Ber.*, 33, 3150.

[2] *Ber.*, 35, 2877.

[3] *Ibid.*, 36, 320, 579.

[4] *Ibid.*, 37, 4709.

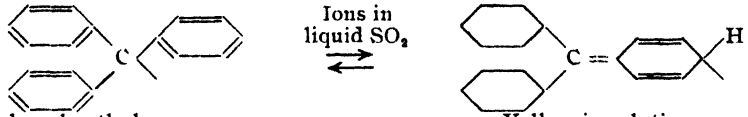
[5] *Ibid.*, 38, 196.

[6] *Ibid.*, 33, 3150; This Journal, 22, 757; *Ber.*, 34, 2726; 35, 1822, 2018, 2397, 3914; 36, 376, 3927; 37, 1626.

[7] *Ibid.*, 37, 2033, 3538.

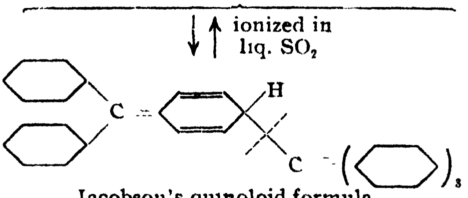
When Gomberg's colorless crystalline substance dissolves in liquid sulphur dioxide a yellow color appears (as in all its solvents). This solution, as Walden[1] and also Gomberg and Cone[2] found, conducts electricity as that of an electrolyte. Gomberg[3] believes at the present time that this remarkable substance is, in the colorless crystalline form, triphenylmethyl, containing the methane carbon in the trivalent state, and the three benzene groups in the usual benzoid form.

When it dissolves, a tautomeric change occurs, one of the phenyl groups undergoes a molecular rearrangement to a yellow quinoloid form, while all three forms exist in equilibrium, in solution. Only the colorless crystalline form separates out when the yellow solutions are evaporated. These changes of triphenylmethyl are here shown.

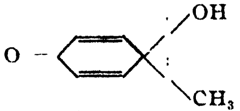


Triphenylmethyl
colorless crystals
(Benzoid form)

Yellow in solution
(Quinoloid form)



Jacobson's quinoloid formula
for triphenylmethyl



Quinol

After Gomberg's brilliant discovery in 1900 there followed in rapid succession the announcements by Professor Norris and Mr. Sanders,[4] and later Kehrmann and Wenzel[5] that the colorless triphenylmethyl hydroxide and chloride dissolve in mineral acids giving colored solutions. Norris and Sanders also discovered the first colored double salt of triphenylmethyl, that of aluminium chloride. These were discoveries of fundamental interest for the development of the theories of color. Later Gomberg and Cone[6] discovered a neutral sulphate as a red crystalline compound and many other colored salts of this type. Other colored salts were made by Baeyer[7] and his co-workers. Salts of these types are shown below.

---

[1] *Z. physik. Chem.*, 43, 443.

[2] *Ber.*, 37, 2045.

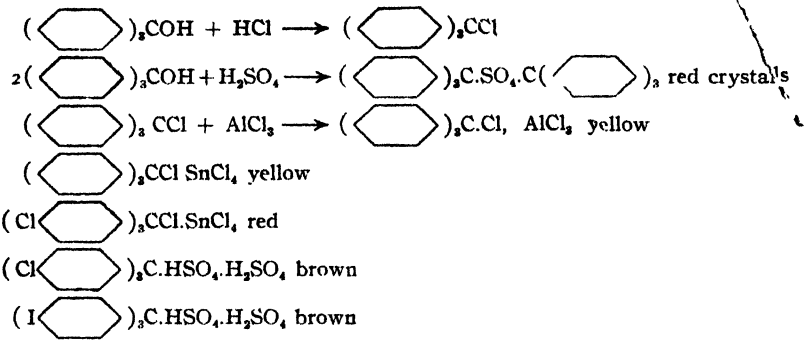
[3] *Ibid.*, 40, 1880–1888.

[4] *Am. Chem. J.*, 25, 54, 117.

[5] *Ber.*, 34, 3815.

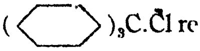
[6] *Ibid.*, 37, 3543, 1626; 35, 1822; 40, 1847, 1872; etc.

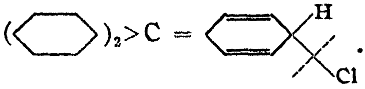
[7] *Ibid.*, 38, 569, 1156; 35, 1199.

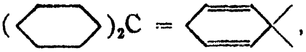

( )$_3$COH + HCl → ( )$_3$CCl
2( )$_3$COH + H$_2$SO$_4$ → ( )$_3$C.SO$_4$.C( )$_3$ red crystals
( )$_3$ CCl + AlCl$_3$ → ( )$_3$C.Cl, AlCl$_3$ yellow
( )$_3$CCl SnCl$_4$ yellow
(Cl)$_3$CCl.SnCl$_4$ red
(Cl)$_3$C.HSO$_4$.H$_2$SO$_4$ brown
(I)$_3$C.HSO$_4$.H$_2$SO$_4$ brown

The old theories of color no longer sufficed. An intense interest was aroused in this whole class of colored derivatives. Baeyer started a very thorough investigation of the entire series of triphenylmethane derivatives, and his work appeared in eleven papers[1] in rapid succession in the *Berichte* and the *Annalen*, from 1902 on.

It is in this field that some of the most interesting color theories, and results, have been worked out.

Why should some of these simple salts of this triphenylmethyl radical be colored and others not? Kehrmann and Wenzel[2] assumed the existence of a colorless, and a colored isomer. The formula  represents the colorless crystalline chloride, while the structure of the isomeric colored salt (and double salts) containing a quinol chromophore are shown thus:



. This last form he considered to be derived from a hydrocarbon, , in which a para position carbon is divalent—very reactive—and has *basic properties.* This idea was contained in Professor Norris' work, which had just appeared. Gomberg holds strongly to this view of structure of all such colored salts and has brought out a large amount of experimental evidence to prove the quinol structure as the cause of color in the whole series of colored triphenylmethane derivatives. The idea of basic carbon has since been worked out by Baeyer, in his *carbonium valence theory*[3] and *halochromy.*[4]

Baeyer,[5] however, took exception to the above quinol formula of Kehrmann for these colored salts. He found chlorine not easily removable by silver salts, as is usually the case in a quinol. To explain the color Baeyer[6] assumed, like Kehrmann, Gomberg and others, a colorless non-

---

[1] *Ber.*, 35, 1189, 1754, 3013 (1902); 36, 2774; 37, 597, 2848, 3191; 38, 569, 1156; 40, 3083; *Ann.*, 354, 152.

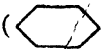
[2] *Ibid.*, 34, 3818.

[3] *Ber.*, 38, 572.

[4] *Ibid.*, 35, 1190, 3014; 38, 1159.

[5] *Loc. cit.*

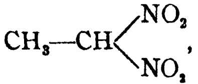
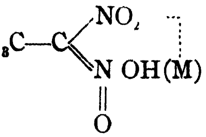
[6] *Ber.*, 38, 571.

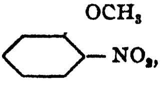
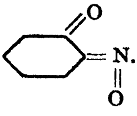
ionizable form, ( )$_3$CCl, and in addition an ionizable colored form, ()$_3$C∼∼∼Cl. To explain the cause of color in these compounds with identical structure and no chromophore group, Baeyer assumed, in the colored ionizable form, a peculiar difference in the properties of a methane carbon valence. This he indicated by a wavy, ionizing bond and called it the "carbonium valence." Like Kehrmann he considered the methane carbon basic, and to behave in such salt formations as the metal in potassium hydroxide. This property of a colorless carbon compound which contains no chromophore group, forming colored salts, he called *halochromy*. This explanation of color was novel, but not altogether satisfactory.

On the whole we find the chief ideas of the cause of color, as at present held by most chemists, to be, for triphenylmethyl and its two series of colorless and colored salts, first a colorless compound of benzoid structure, second—its molecular rearrangement to a colored form, having a quinone or a quinol structure, this unsaturated quinol ring being the chief cause of the color.

Let us turn to a new field.

The same general causes of color phenomena, namely, the change of a colorless compound into an isomeric colored form by a molecular rearrangement, Hantzsch found to exist in the nitrohydrocarbons, nitroketones,[1] and nitrophenols.

Colorless dinitroethane,[2]  $CH_3{-}CH\begin{matrix}NO_2\\NO_2\end{matrix}$, dissolves in sodium hydroxide with a yellow color. This color Hantzsch supposed to be due to a salt of a compound of a tautomeric form,  $H_3C{-}C\begin{matrix}NO_2\\N\,OH(M)\\\|\\O\end{matrix}$, which contains a chromophore, and in which there is a union of some sort between the nitro groups.

Such colorless substances which yield colored salts he classed among the *pseudo acids*.[3] This view of changing structure as the cause of color is confirmed by Hedley's[4] spectroscopic studies of nitroparaffins and their salts. After years of work on nitrohydrocarbons, Hantzsch was able to prove this theory. In 1906, Hantzsch and Gorke[5] obtained such isomers, not as metal salts, but as esters of nitrophenols. The formulas show this type, one colorless,  and the other intensely red,  Here at last was the confirmation of his theory of pseudo acids, for these crystalline esters of identical composition and like molecular weight, but differi in color, cannot have the same structure. This discovery was also important addition to our knowledge of the relation of color to chemic constitution. It also proved[1] the falsity of Oswald's theory[2] that the col of salts of such colorless compounds as phenolphthalein is *primarily* d to the formation of colored ions. Additional proof that such color chang are rather due to a molecular rearrangement has been well given t Hantzsch's[3] work on helianthin and methyl orange, and that of Vorlände Thiele,[5] and Hantzsch and Hilscher[6] on aminoazobenzenes and their tw series of colored salts.

---

[1] *Ber.*, 40, 1523.

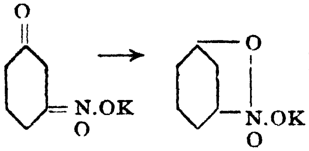
[2] *Ibid.*, 32, 578, 610, 626; 39, 3156; 40, 1533.

[3] *Ibid.*, 32, 578, 579, 583; 35, 1001.

[4] *Ibid.*, 41, 1195.

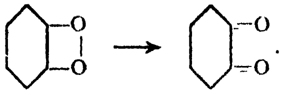
[5] *Ibid.*, 39, 1073.

Hantzsch and Rosanoff[7] obtained isomeric colored salts of substitute metanitrophenols. One was lemon-yellow and unstable, easily changin into a stable red isomer. The structures have been suggested for these isomeric colored salts, though the question is a complicated one and remains unsettled.



Yellow salt Red salt

The existence of these two forms of metanitrophenol salts suggests the possibility of the existence of metaquinones—as well as two forms of *o*-benzoquinone. The latter were in reality found last year by Willstätter,[8] one labile and colorless, and readily changing to the other stable and colored form.



Colorless labile Yellow stable
orthoquinones.

Hantzsch and his co-workers extended these researches very widely over a period of several years and from a large amount of experimental data drew the following conclusion: All true nitro compounds of the hydrocarbons and derivatives are colorless.[9] The nitro group is *not* a chromophore. Its presence in a molecule only gives color when it interacts with a neighboring group containing a labile hydrogen atom, as the OH or CH group, whereby a tautomeric form is created which contains a chromophore group—yielding colored salts and esters. Kaufmann,[10] however, opposes this theory. Hantzsch makes this of general application in his statement as follows: "Every appearance of, or change of, color of a

[1] *Ber.*, 39, 1089, 1091.

[2] *Die Wissenschaftliche Grundlagen der analytischen Chemie*, 1894, p. 104.

[3] *Ber.*, 41, 1187, 1193.

[4] *Ibid.*, 36, 1486.

[5] *Ibid.*, 36, 3965.

[6] *Ibid.*, 41, 1171.

[7] *Ibid.*, 39, 1073, 1084; 40, 1535.

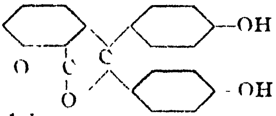
[8] *Ibid.*, 41, 2580.

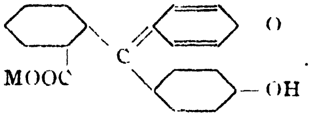
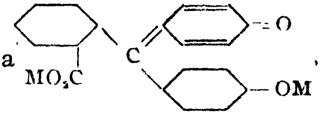
[9] *Ibid.*, 39, 1084, 1096.

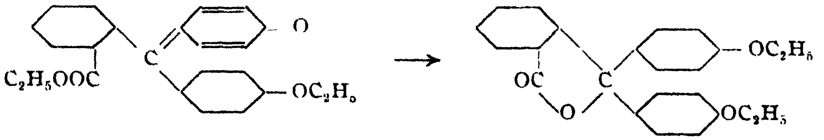
[10] *Ibid.*, 39, 1959, 4237.

compound in salt formation with colorless metal atoms is to be ascribed to an intramolecular rearrangement." Such a phenomenon as indicated here he calls *chromotropy*, and the isomeric substances, *chromoisomers.*

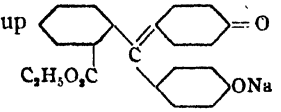
An interesting application of this chromotropic theory is to those compounds, like phenolphthalein, methyl orange, aminoazobenzene, and others, which rapidly undergo color changes in salt formation in solutions.

The formula  shows Baeyer's lactone structure for phenolphthalein.

The well-known violet-red color of a phenolphthalein solution, when alkali is added, was supposed by many to be due to a monobasic salt, . In 1905 Meyer and Spengler[1] succeeded in separating and analyzing the red salt and found it dibasic, but considered its color due to halochromy. Baeyer[2] who also held this view of color rejected it in 1907, as did also Richard Meyer[3] last July in favor of the quinoid structure and tautomerism in the salts, as a cause of the color in phenolphthalein solutions. This idea had previously been suggested by Stieglitz and Acree.[4] Friedlander[5] had in 1893 assumed the presence of a red dibasic salt and had suggested the formula , which contains a quinoid ring, as the cause of color. Richard Meyer and Marx[6] showed, two years ago, that the production of color in colorless phenolphthalein solutions was due to a molecular rearrangement and the formation of a quinoid group. They were not able to show this in the salts, but with the corresponding esters. These they obtained in isomeric form and assigned the following structure to the yellow unstable one, which easily changes over to the colorless stable form, which contains no chromophore group:



Yellow crystals, labile Colorless crystals, stable

In this they indicated the tautomeric character of the change during color formation with phenolphthalein solutions. The color reactions and formation of colored esters in phenolphthalein cannot, however, be fully explained by the mere *presence* of the quinoid ring alone as chromophore. Arthur Green[1] in a recent paper (June last) has called attention to the fact that if, in this yellow quinoid ester, sodium be substituted for the ethyl radical in the phenol group  a very deep violet-red color is produced. This decided deepening of color cannot be due to the sodium atom as such, as it is not a chromophore, but in some way to its interrelation to the neighboring quinoid ring; in other words *the phenol and quinoid groups interact* as a strong chromophore. Such interaction of groups was proposed by Dr. Stieglitz[2] in his quinhydrone theory, to explain color formation, not only in phenolphthalein, but also in the rosanilines, rosolic acids, and eosins. He believed the presence of a quinone and a phenol group gave color by virtue of an intra- or intermolecular condensation, forming quinhydrones, compounds whose salts have intense colors, as we shall soon note below.

---

[1] *Ber.*, 38, 1318; 41, 2446.

[2] *Ann.*, 354, 152.

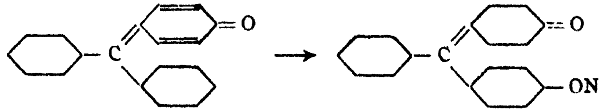
[3] *Ber.*, 42, 2832.

[4] *Am. Chem. J.*, 39, 543, 650 and 651.

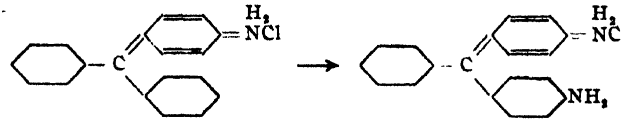
[5] *Ber.*, 26, 172.

[6] *Ibid.*, 40, 3603.

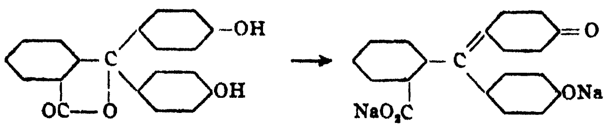
Baeyer[3] has recently discussed similar cases of color intensification. Oxo- and imino-triphenylmethane (the former called fuchsone) are only faintly colored orange, but an intense deepening of color is produced by simply introducing an hydroxyl, and an amine group respectively, in an adjacent phenyl group, and forming salts.



Fuchsone, orange **Benzaurin, violet-red**



Iminotriphenylmethane (salt), orange **Döbner's violet, violet-red**



Phenolphthalein, colorless **Salt, violet-red**

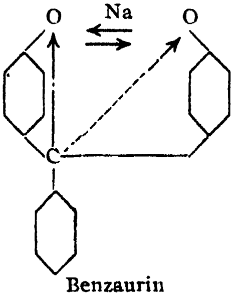
The mere presence of these added groups can neither explain this deep color change, nor the remarkable fact that the red salts have indentical absorption spectra—and therefore, identical color. They are also, in this respect, identical with the red salts of phenolphthalein. This is a very strong argument in favor of like structure in all three compounds. Such similarity of structure is not shown in the above formulas. Baeyer has, however, sought to indicate it[1] by assuming a rapid oscillatory change of the quinoid structure from one ring to the other, involving a corresponding movement of both the sodium or chlorine atom from oxygen to oxygen or nitrogen to nitrogen, respectively—and likewise an oscillation of a carbon to oxygen, or nitrogen, valence, as shown below:

---

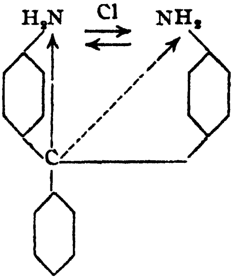
[1] *J. Chem. Ind.*, 28, 638.

[2] *Am. Chem. J.*, 39, 651, 529, 431.

[3] *Ann.*, 354, 152.



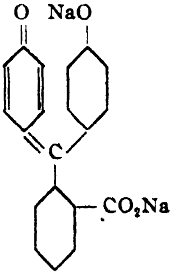
Benzaurin



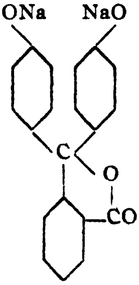
Döbner's violet

An auxochrome group is here shown to act not by its presence only, but by its interrelation or action with the rest of the molecule. This has also been clearly shown by Hantzsch[2] in the colored salts and esters of the colorless nitrophenols.

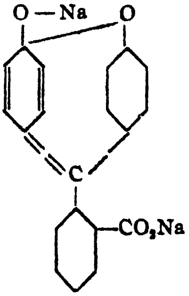
In interesting papers in the *American Chemical Journal* of April, 1908, and July of the present year on the subject of indicators, Acree and Slagle[3] assert that in addition to such quinoid and lactoid dibasic salts of phenolphthalein as shown here,



Quinoid



Lactoid

a third form exists,  , to which the color may be largely

---

[1] *Ann.*, 354, 152.

[2] *Ber.*, 39, 1073, 1084; 40, 1535.

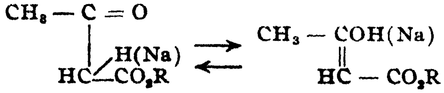
[3] *Am. Chem. J.*, 42, 122.

Absorption bands in	Color of substance is
Ultraviolet	———
Violet	Green-yellow
Indigo	Yellow
Blue	Orange
Blue-green	Red
Green	Purple
Green-yellow	Violet
Yellow	Indigo
Orange	Blue
Red	Green-blue
Purple	Green
Ultrared	———

The absorbed color is the complement of the color apparent to eye.

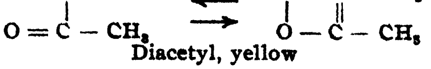
Baeyer's explanation of the intense color caused by salt formation in benzaurin and Döbner's violet as shown in the above formulas is an extension of Hartley's idea of intramolecular vibration and of the idea of isorropesis.

Equally interesting are the researches of Stewart, Baly and Desch.[1] They studied the absorption spectra of many unsaturated compounds, among them tautomeric substances which have a labile hydrogen atom capable of wandering to an adjacent carbon or oxygen atom. Such is acetoacetic ester, and its sodium salt, which have the tautomeric forms:



$$\begin{array}{l} CH_3 - C = O \\ \quad | \\ HC\begin{smallmatrix}H(Na)\\CO_2R\end{smallmatrix} \end{array} \rightleftarrows \begin{array}{l} CH_3 - COH(Na) \\ \quad \| \\ HC - CO_2R \end{array}$$

They found[2] in such compounds, and their tautomeric derivatives, that either form alone had little effect on the spectrum, but when light was passed through a solution in which both were present in tautomeric equilibrium, that characteristic absorption bands appeared. From this they concluded that it is not the fixed structure of a desmotropic molecule which causes absorption, but that it is due to the rapid oscillating change of atomic linking which occurs as a molecule changes from one form over to the other and reverses, which causes vibrations synchronous with certain light waves which thereby become absorbed, giving absorption spectra and consequently color. This rapid oscillating vibration of the valences, when unaccompanied by tautomeric atomic movement, they have called *isorropesis*[3] (equipoise). It can be most simply illustrated in the case of diacetyl or oxomalonic ester, in which the rapid oscillating change of double bonds between adjacent carbonyl groups is shown. It is not supposed that such isomeric forms really exist, but that the formulas represent the *limiting conditions* of such dynamic changes within a molecule of such a colored substance.



$$\begin{array}{l} O = C - CH_3 \\ \quad\ | \\ O = C - CH_3 \end{array} \leftrightarrows \begin{array}{l} O - C - CH_3 \\ |\quad\ \| \\ O - C - CH_3 \end{array}$$

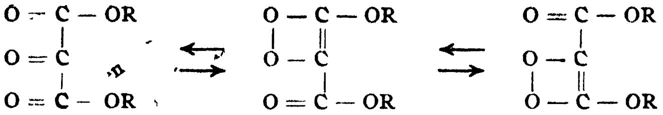
Diacetyl, yellow

---

[1] *J. Chem. Soc.*, 85, 1029; 87, 766; 89, 502, 514, 618; 91, 426, 1572; *Proc. Chem. Soc.*, 22, 33, 34, 35 (1906).

[2] *J. Chem. Soc.*, 85, 1029, 1039; 89, 489.

[3] *Ibid.*, 89, 498, 513.



Oxomalonic ester, green.

If we consider, then, these interesting optical results in the light of our present ideas of the constitution of the atoms, we should seek the *final* cause of color, in a disturbance of the equilibrium of electrons within the atoms, induced by the breaking of the Faraday tubes of force between the atoms. This is represented by our bonds or valence lines undergoing rapid oscillatory changes as suggested in the formulas above. We might well expect such a disturbed equilibrium to produce or annul ether vibrations of the order of those which produce color, and thus account for the absorption bands in the spectra of numberless organic compounds showing visible as well as invisible color.

UNIVERSITY OF ILLINOIS,
URBANA, ILL.

NOTES.

The Instability of Alloxan.—On returning to the Chemical Laboratory after the summer vacation last year I found that an explosion had taken place in the case of specimens of organic chemicals in the lecture room. A pane of glass was pierced by a round hole as large as my fist and pieces of glass had been forcibly projected against the opposite wall of the room, ten feet from the case. Within the case quite a number of bottles were ruined. A careful examination of them showed very plainly that a bottle of alloxan containing 10 grams had been the cause of the wreck. This sample of alloxan had been in the case for several years and the past summer was an unusually cool one. I was not aware that alloxan had any such property and have been unable to find that it is subject to any such behavior. ALVIN S. WHEELER.

UNIVERSITY OF NORTH CAROLINA

The above note by Professor Wheeler on the instability of alloxan is of peculiar interest to the writer.

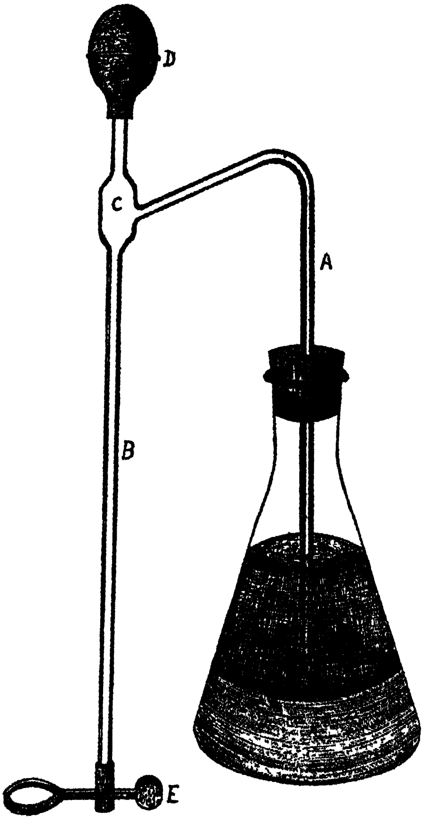
Several years ago, upon my return to the laboratory at the close of the summer vacation, I found that an explosion had occurred in one of our cupboards for fine organic chemicals. The force of the explosion shattered all the neighboring bottles on that end of the shelf, so that it was impossible to tell which particular bottle was responsible for the trouble. We checked up all the missing bottles by our shelf list, but among those destroyed there were none that we had ever heard mentioned as likely to decompose with explosive violence, and the matter remained very much of a mystery. Prof. Wheeler's article seems to solve this mystery, for among the wreck and ruin of broken glass in our cupboard were found portions of a bottle of alloxan which, according to our shelf list, hould have been standing about where the explosion occurred.

MARSTON TAYLOR BOGE

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY

An Improved Siphon.—In our laboratory practice we have felt the need of a more efficient siphon than is now found on the market. In an effort to improve upon this form of apparatus, we have constructed a small glass siphon that combines simplicity of construction and ease of manipulation, and is especially adapted to extraction work with non-miscible solvents.

The siphon is really nothing more than a branched pipette, with the branch entering the bulb of the pipette as represented in the figure. The branch arm *A* consists of heavy capillary tubing with a 2 mm. bore, while the other glass parts are made of the ordinary thin glass. The bulb *C* has a capacity of 5 cc., which is ample for ordinary operations. Tube *B* is 22 mm. long, having an internal bore of 3 mm. The lower end of this tube is fitted with a short piece of rubber tubing, and is opened or closed by means of a small spring clamp. The upper end of the siphon is fitted with a small rubber bulb. Tube *A* is fitted with a cork having a vertical slit along the side, and fitting the separatory funnel or flask containing the liquid to be siphoned.



To operate the siphon, tube *A* is introduced into the liquid. The rubber bulb *D* is compressed, and the clamp at *E* closed. By gently releasing the pressure on the bulb, enough of the liquid will be drawn into *B* to start it to siphoning when clamp *E* is opened.

No other support, besides the cork, is necessary to hold the siphon in position. The hole through the cork should be large enough to permit the siphon to be raised or lowered during the operation. Tube *A* is made of heavy glass to give firmness to the siphon, and has a small bore to allow every drop of liquid in it to be transferred.

This form of siphon not only can be operated rapidly and conveniently, but it eliminates the danger of drawing the liquid into the mouth, or breathing offensive and poisonous vapors, which sometimes happens with the ordinary form of siphon.

Where it is absolutely necessary to avoid all contact with rubber, a piece of paraffin or wax may be pressed against the opening of the tube at *E*, until *B* is filled. A glass stopper might be inserted at *E*, but we consider that unnecessary.

The siphon is not only adapted for the removal of solution extracts but is applicable for the removal of supernatant liquids, where decantation would disturb the precipitate at the bottom; or for drawing off standard solutions, reagents, etc. It is especially convenient when colloidal solutions are to be filtered, or where one filtration requires several hours. In such cases the flow through the siphon is regulated by means of a chip of wood, holding the spring clamp open, so that the drip through the siphon equals that through the filter.

C. A. JACOBSON AND S. C. DINSMORE.

NEVADA AGRICULTURAL EXPERIMENT STATION,
RENO, NEVADA.

NEW BOOKS.

Neuvième Congrès International de Géographie. GENÈVE. 27 Juillet-6 Août, 1908. Compte Rendu des Travaux du Congrès. T. I. Organisation du Congrès. II. Travaux Scientifiques. A. Séances Générales. Genève, 1909. pp. xv + 475; pl. v; Figs. 15.

This report contains an account of the organization of the 9th International Geographic Congress held at Geneva in the summer of 1908. The character of the Congress is indicated by the fact that it was attended by 303 delegates, representing 24 governments, 32 universities, 81 geographical societies, and a number of other scientific organizations. In addition to the numerous social functions enjoyed by the membership in general, a large number of excursions and conferences were participated in by small groups of members. The number of papers read before the Congress was naturally great, but only a few possess any but a geographic interest. Only the non-technical ones appear in the volume under review. Of these the paper of most general interest is that by A. Penck, in which an account is given of the gratifying progress made toward securing a map of the entire world on the uniform scale of 1 : 1,000,000.

W. S. BAYLEY.

Wall Charts for Sugar Chemists: I. *Table for Finding the Sucrose Content of Juices,* clarified with 10 per cent. of subacetate of lead from the specific gravity of the original juice, and the readings in a Schmidt and Hänsch polariscope when observed in a 200 mm. tube. II. *Tables for the Correction of the Brix Hydrometer at Different Temperatures.* (*a*) When the hydrometer is tested at 84° F. (*b*) When the hydrometer is tested at 17.5° C. Published by NORMAN RODGER, Altrincham, England. Price 5/-net for the two, or 3/-net for either. Foreign postage 6d extra.

The subject matter of these two charts is familiar to every sugar chemist having been taken from Prinsen Geerligs' "Methods of Chemical Control in Cane Sugar Factories." The larger chart for finding the sucrose content of juices has a range of 0.5 to 24° Brix for polariscope readings extending from 1 to 90, the sucrose content for these limits ranging from 0.29 per cent. to 23.41 per cent. The smaller chart for correcting Brix hydrometers has a range of corrections for readings from 0° to 75° Brix for temperatures extending from 15° C. to 100° C. and 60° F. to 212° F. The two charts are mounted upon cloth and suitable for hanging upon the wall of laboratory or office. This new arrangement of Mr. Geerligs' excellent tables will be found a great convenience to the sugar chemist.

C. A. BROWNE.

Le Cinquantenaire de l'atomecanique ou de la Mécanique des atomes. I. *Quelques lettres de quelques Collèques Membres de l'Institut.* II. *Supplément.* III. *Fragments inédits.* By GUSTAVUS D. HINRICHS, St. Louis, Missouri. 64 pp. 4°; illustrated.

This brochure contains excellent pictures of a number of eminent chemists who have written to the author from time to time and facsimiles of some of their letters. The supplement gives extracts from a number of Professor Hinrichs's publications of the past half century. In the fragments several diagrams illustrating the author's method of calculating atomic weights are published for the first time.

W. A. N.

Manuel théorique et pratique d'analyse volumétrique. PAR LOUIS DUPARC, Professeur de minéralogie et de chimie analytique et Directeur des laboratoires d'analyse minérale de l'Université de Genève, et MARIA BASADONNA, Privat docent à l' Université. Avec 12 figures. 8vo, 170 pp. 1910. Paris: Felix Alcan.

This book is primarily designed for the instruction of pupils in the laboratory, a fact which probably accounts for the omission of nearly all matters of theory or of an explanatory character. A clear definition of normal solutions and brief descriptions of the most important volumetric apparatus are given and about two pages are devoted to the calibration of the latter. The analytical methods chosen for presentation are well selected and the descriptions are as lucid as is compatible with the highly condensed form of presentation adopted throughout. Many readers will regret that the author has restricted himself to one method for the standardizing of each solution, thus providing for no control over the accuracy of the work. Indeed, standardizing is sometimes omitted entirely, except by the second-hand way of comparison.

A surprisingly large number of individual determinations are described, considering the modest size of the volume, and are given in sufficient detail to serve as a needed reminder to one who has previously used the methods. The very short account of the theory of indicators entirely ignores the important work of the last five years, which has for the first time cleared up the main questions involved.

The work is very suitable for use in conjunction with thorough class instruction and may be welcomed as filling a field not yet satisfactorily occupied by other treatises comparable with it in size. There is no index, but only a tolerably full table of contents. L. W. Andrews.

RECENT PUBLICATIONS.

Armstrong, E. F.: **The Simple Carbohydrates and the Glucosides.** London: Longmans, Green & Co. 110 pp., 3 s. 6 d.

Bertelsmann, W.: **Rechentafeln für Beleuchtungstechniker.** Stuttgart: 8°, 95 s., 2.6 M.

Böhm, C. R.: **Die Fabrikation der Glühkörper für Gasglühlicht.** Halle a/S: W Knapp. 8°, 454 s., 23 M.

Bruce, J., and Harper, H.: **Practical Chemistry.** Macmillan: 248 pp., 2 s., 6 d.

Bruner, L. und Vorbrodt, J.: **Einfluss der Lösungsmittel auf die Verteilung der Isomeren.** Krakau: 18 s., 0.80 M.

Clennell, J. E.: **The Chemistry of Cyanide Solutions Resulting from the Treatment of Ores.** Second edition. New York: McGraw-Hill Co. 202 s., $2.50.

Dessau: **Die physikalisch-chemischen Eigenschaften der Legierungen** (Heft 33 von "Die Wissenschaft"). Braunschweig: 8 M.

Ehrsam, H.: **Fabrication des huiles minérales et pyrogénées.** Paris: 8°, 8.50 M.

Hahn, H.: **Chemie für Techniker. 2 Bd. Organische Chemie.** Hannover: M. Jänecke. 3.2 M.

Hammarsten, O.: **Lehrbuch der Physiologischen Chemie.** 7 Aufl. Wiesbaden: 8°, 23 M.

Heim, M.: **Steingutfabrikation.** Hannover: M. Jänecke. 4 M.

Hort, H.: **Der Entropiesatz oder der zweite Hauptsatz der mechanischen Wärmetheorie.** Berlin: 8°, 41 s., 1 M.

Javillier, M.: **Les Ferments protéolytiques. Etude chimique et pharmacotechnique.** Paris: 8°, 5 M.

Jurisch, K. W.: **Ueber Luftsalpeter.** Leipzig: 8°, 1.50 M.

Kirchner, O.: **Die kaustische und kohlensaure Verseifung in der modernen Seifenindustrie. Die Haushaltungsseife.** Wien: A. Hartleben. 4.80 M.

Krönlein, H.: **Lederfabrikation.** Hannover: Dr. M. Jänecke. 3.50 M.

Latta, M. N.: **American Producer Gas Practice and Industrial Gas Engineering.** New York: D. Van Nostrand. 8°, 550 pp., $6.00.

Lavaux, J.: **Sur une association naturelle de dimethylanthracènes.** Paris: 161 s.

LEHMANN, O.: **Flüssige Krystalle, Myelinformen und Muskelkraft.** chen: 8°, 43 s., 1 M.

MANNHEIM, E.: **Toxikologische Chemie.** Leipzig: 8°, 155 s., 0.80 M.

MITREITER, M.: **Die Gewinnung des Broms in der Kaliindustrie.** Halle S: 24 s., 2 M.

MOLL, R.: **Beitrage zur Biochemie des Bodens.** Leipzig: 8°, 58 s., 2 M.

PLOTNIKOW: **Photochemie.** Halle a/S: 7.50 M.

PÖSCHL, V.: **Einführung in die Kolloidchemie. Abriss der Kolloidchemie.** 2 Aufl. Dresden: 8°, 70 s., 1.80 M.

POULIEN, A.: **Zement im Meerwasser.** Kopenhagen: 8°, 68 s., 3.60 M.

RENGADE, E.: **Analyse thermique et métallographie microscopique.** Avec un préface de H. Le Chatelier. Paris: 8°, 176 s.

RICKE, R.: **Porzellan.** Hannover: Dr. M. Jänecke. 4 M.

SANG, A.: **The Corrosion of Iron and Steel.** Hill Publ. Co. 8°, 4 s., 6 d.

SCHLOSSMANN, A.: **Leitfaden der Milchhygiene.** Leipzig: O. Nemnich. 10 M.

SCHEFFLER, W.: **Einrichtung eines Fabriklaboratoriums.** Hannover: Dr. M. Jänecke. 4.50 M.

SCHIPPMAN, W.: **Aus der Praxis eines Glashüttenfachmannes.** Hannover: Dr. M. Jänecke. 3.60 M.

SCHMIDT, J.: **Der Aether und seine Aggregatzustande.** Elberfeld. 8°, 71 s.

SHERFESEE, W. F.: **Wood Preservation in the United States.** Washington: U. S. Dept. of Agriculture. 31 pp.

WEDEKIND, E., UND LEWIS, J.: **Neue Atomgewicht-Kurven.** Stuttgart: F. Enke. 21 s., 1.60 M.

WODISKA, J.: **Book of Precious Stones. Identification of Gems and Gem Minerals and Account of their Scientific, Commercial and Artistic Aspects.** London: 8°, 382 pp., 11 M.

JULY, 1910. No. 7.

THE JOURNAL

OF THE

American Chemical Society

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 50.]

QUANTITATIVE APPLICATION OF THE THEORY OF INDICATORS TO VOLUMETRIC ANALYSIS.

BY ARTHUR A. NOYES

Received May 4, 1910.

Contents.

I. GENERAL CONSIDERATIONS: 1. Purpose of the Article. 2. The Chemical Nature of Indicators. Equilibrium Relations of the Tautomeric Forms. 3. Equilibrium Relations of Indicators with Reference to the End-Point of Titrations. 4. Experiments Illustrating the Relation between the Color-Change of Indicators and the Hydrogen Ion Concentration. 5. Discussion of the Indicator-Function. 6. Concentration of the Indicator.

II. TITRATION OF MONOBASIC ACIDS AND MONACIDIC BASES: 7. General Formulation of the Theory. 8. The Error in the Titration. 9. Error in the Titration when a Neutral Salt is Originally Present. 10. The Best Value of the Indicator-Function. 11. Limiting Values of the Indicator-Function. 12. Limits beyond which the Titration is Impracticable.

III. TITRATION OF TWO MONOBASIC ACIDS OR OF TWO MONACIDIC BASES IN THE PRESENCE OF EACH OTHER: 13. Separate Titration of the More Ionized Acid. 14. Separate Titration of the More Ionized Base. 15. Titration of the Less Ionized Acid or Base.

IV. TITRATION OF DIBASIC ACIDS WITH MONACIDIC BASES: 16. General Formulation of the Theory. 17. Error in the Titration of the First Hydrogen. 18. Best Value and Limiting Values of the Indicator-Function for Titration of the First Hydrogen. 19. Error in the Titration of the Total Hydrogen. 20. Best Value and Limiting Values of the Indicator-Function for Titration of the Total Hydrogen.

V. TITRATION OF DIACIDIC BASES WITH MONOBASIC ACIDS: 21. Error in the Titration of the First Hydroxyl. 22. Best Value and Limiting Values of the Indicator-Function for Titration of the First Hydroxyl. 23. Titration of the Total Hydroxyl.

VI. SUMMARY: 24. Summary.

VII. APPENDIX: 25. Values of the Ionization-Constants of Indicators. 26. Values of the Ionization-Constants of Acids and Bases.

I. General Considerations.

1. *Purpose of the Article.*—Although the explanation of the behavior of neutralization indicators, originally given by Ostwald,[1] was one of the early triumphs of the Ionic Theory, and although many investigations upon indicators from a physico-chemical standpoint have since been made, yet the quantitative development of the theory of indicators in a systematic form immediately applicable to the problems of volumetric analysis seems not to have been undertaken.[2] It is the purpose of this article to present such a development.

The following discussion, owing to the large number of factors and special cases to be considered, unfortunately involves a somewhat lengthy, though comparatively simple, mathematical treatment. The reader who is interested in the results, rather than the method of derivation, is therefore recommended, after reading Sections 3 and 5 of this Part of the article, to pass directly to the Summary at the end, in which an attempt has been made to present the conclusions fairly completely and connectedly in a form in which they can be directly applied to the problems of volumetric analysis.

2. *The Chemical Nature of Indicators. Equilibrium Relations of the Tautomeric Forms.*—The original explanation of the behavior of indicators suggested by Ostwald was based on the simple hypothesis that the slightly ionized indicator acid or base has a different color from that of its ionized salt, into which it is converted by the addition of alkali or acid. More recent work has, however, shown that this explanation is inadequate in view of the well-known relations between the color and the structure of organic compounds, and in view of the results of the special investigations of Bernthsen, Nietzi and Burckhart, Hantzsch, and others on tautomeric colored substances.[3] It is in all probability true that a neutralization indicator always consists of tautomeric substances[4] of two different structural types possessing different colors, one of which types greatly predominates when the indicator exists as a slightly ionized acid or base, and the other when it exists as a largely ionized salt. Thus, the indicator may consist of a mixture of two tautomeric acids, HIn′ and HIn″, the equilibrium between these two acids being such that the acid HIn′ is present in greatly predominating quantity. Owing to the fact, how-

---

[1] *Lehrbuch der allgemeinen Chemie*, 1, 799 (1891). See also his *Wissensch. Grundlagen der anal. Chemie*, 3rd edit., pp. 117–23 (1901).

[2] It should be mentioned, however, that a brief treatment of a part of the problem has already been given by McCoy (*Am. Chem. J.*, 31, 512–6 (1904)), and by Salm (*Z. physik. Chem.*, 57, 497 (1907)).

[3] For a discussion of this matter, see Stieglitz, THIS JOURNAL, 25, 1112–20 (1903).

[4] From the modern standpoint tautomeric substances may be defined as isomeric substances which tend to go over into each other directly in one direction or the other until equilibrium is reached.

ever, that the acid HIn'' has a very much larger ionization-constant, its salt is formed in much larger proportion than that of the other acid when the mixture is neutralized with a base. Hence a change in color takes place in correspondence with the different structural type which predominates in the acid and alkaline solution. It has been shown by Stieglitz[1] that the conditions just stated do not make necessary any substantial modification of the equilibrium relations of indicators, so far as their behavior in titrations is concerned.

Since the limitations just mentioned with reference to the relative concentrations of the different forms are not in all cases necessary, it seems desirable to treat the matter from a somewhat more general standpoint, as follows.

Let us consider an acid indicator composed of two tautomeric substances, HIn' and HIn'', which when neutralized with a base BOH are converted into the corresponding salts BIn' and BIn'', these being largely dissociated into the ions B^+, In'^- and In''^-. In order that an indicator may be satisfactory in the respect that it show a sharp color-change on neutralization, it is evidently essential that the following conditions be fulfilled: (1) One of the structural forms must be colorless and the other colored; or else, the two structural forms must be of distinctly different colors. (2) Either form that may be colored must not exist in appreciable proportion in both acid and alkaline solutions.

In accordance with these general conditions, the three following cases may occur, the convention that the indicator shows in acid solution the color corresponding to the form HIn' being employed in their formulation:

(*a*) The indicator is colorless in acid and colored in alkaline solution. Hence HIn', BIn', and In'^- are colorless; HIn'', BIn'', and In''^- are colored; and $(HIn'')/(HIn')$[2] must be very small.

(*b*) The indicator is colored in acid and colorless in alkaline solution. Hence HIn', BIn', and In'^- are colored, HIn'', BIn'', and In''^- are colorless, and $(In'^-)/(In''^-)$ must be very small.

(*c*) The indicator has two sharply differentiated colors in acid and alkaline solution. Hence HIn', BIn', and In'^- have one color; HIn'', BIn'', and In''^- have a different color; and both $(HIn'')/(HIn')$ and $(In'^-)/(In''^-)$ must be very small.[3]

Corresponding criteria for a satisfactory color-change can also be readily formulated for the case of a basic indicator existing in alkaline solution in the two structural forms $In'OH$ and $In''OH$, which when neutralized with an acid HA are converted into the corresponding salts In′A and In″A, these being largely dissociated into the ions In'^+, In''^+, and A^-. It is not, however, necessary to formulate these conditions here.

---

[1] *Loc. cit.*, p. 1122.

[2] Throughout this article symbols enclosed within parentheses denote the molar concentrations of the substances represented by the symbols.

[3] For evidently, if there were present a considerable proportion of HIn'' in the acid solution, or of In'^- in the alkaline solution, a mixed color corresponding to the superposed colors of the two structural forms would result.

We may next derive a general expression (as has previously been done by Acree[1]) for the equilibrium-relations of any pair of tautomeric acids and their ions. The three fundamental equilibrium equations are as follows:

$$\frac{(H^+)(In'^-)}{(HIn')} = K_I'; \quad (1) \qquad \frac{(H^+)(In''^-)}{(HIn'')} = K_I''; \qquad (2)$$

and

$$\frac{(HIn'')}{(HIn')} = K_T. \qquad (3)$$

Multiplying (2) by (3), adding (1) to the product, and substituting in the denominator for (HIn′) its value $\frac{(HIn') + (HIn'')}{1 + K_T}$ given by

get:

$$\frac{(H^+)[(In'^-) + (In''^-)]}{(HIn') + (HIn'')} = \frac{K_I' + K_I''K_T}{1 + K_T} = K_{IA} \qquad (4)$$

If the indicator is a base existing as the two tautomeric substances In′OH and In″OH, having ionization constants K_I' and K_I'' and a tautomer constant K_T defined by equations analogous to (1), (2), and (3), the general expression for the equilibrium between the ionized bases and their ions is:

$$\frac{(OH^-)[(In'^+) + (In''^+)]}{(In'OH) + (In''OH)} = \frac{K_I' + K_I''K_T}{1 + K_T} = K_{IB} \qquad (5)$$

In these expressions a single constant K_{IA} or K_{IB} has been introduced in place of the function of the three constants K_I', K_I'', and K_T. This constant K_{IA} or K_{IB} will throughout this article be called simply the ionization-constant of the indicator acid or base.

The constant so calculated for a pair of tautomeric acids or bases can evidently be substituted for the ionization-constant of an ordinary (non-tautomeric) acid in any derived expression, provided the *sum of the* two ion-concentrations and the *sum* of two acid or base concentrations are the quantities that are known or are to be calculated. Thus the ionization-constant for a pair of tautomeric acids or bases as determined by conductance measurements would be that expressed by equation (4) or (5), since it is the sum of the ion-concentrations that are determined by such measurements. So also the degree of hydrolysis *h* of the sodium salts of a pair of tautomeric acids would be expressed, like that of the salt of an ordinary acid, by the familiar equation,[1] $\frac{\gamma_B h^2 C}{\gamma(1-h)} = \frac{K_W}{K_A}$, provided K_A, the ionization-constant of the tautomeric acids, be calculated by an expression of the form of equation (4); for it is the sum of the two forms of the acid that corresponds to the hydrolyzed portion, and it is the sum of the two forms of the salt that corresponds to the unhydrolyzed portion.[2]

---

[1] *Am. Chem. J.*, 38, 19 (1907).

Equations (4) and (5) can evidently be used to express the color changes exhibited by indicators or other tautomeric substances when, and only when, the intensity of the color is substantially proportional to the sum of the concentrations of the two tautomeric acids or bases, or to the sum of the concentrations of the two tautomeric ions. It has already been seen, however, that for a satisfactory two-color acid indicator (case *c*) the sum $(\text{HIn}') + (\text{HIn}'')$ must be substantially identical with (HIn') and the sum $(\text{In}') + (\text{In}''^-)$ substantially identical with (In''^-). It has also been seen that for a satisfactory one-color acid indicator (case *a* or *b*) either the former or the latter of these two identities must hold true; and it may now be pointed out that the intensity of the color is proportional to the other sum involved, namely to $(\text{In}'^-) + (\text{In}''^-)$ in case *a*, and to $(\text{HIn}') + (\text{HIn}'')$ in case *b*. This follows from the fact that these sums are proportional, in virtue of equations (1), (2), and (3), to (In''^-) and to (HIn') respectively, which are the substances on which the color alone depends in the two cases. From this it follows, in case *a* for example, that the ratio, of the color intensity of the indicator when partially transformed into its salt, to its color intensity when completely transformed, is equal to the ratio of the sums of the concentrations of the colored and colorless salts in the two cases. Similar conditions prevail in the case of two-color and one-color basic indicators.

Equations (4) and (5) may therefore be employed to express the equilibrium relations and color relations of such indicators as are included under cases *a*, *b*, and *c* described above and under the corresponding cases applicable to basic indicators—that is to say, of such indicators as can show a sharp color-change on neutralization. These equations will therefore be made the basis of the considerations presented in the next section; but for greater simplicity, (In^-) will hereafter be written for $(\text{In}'^-) + (\text{In}''^-)$, (HIn) for $(\text{HIn}') + (\text{HIn}'')$, (In^+) for $(\text{In}'^+) + (\text{In}''^+)$, and (InOH) for $(\text{In}'\text{OH}) + (\text{In}''\text{OH})$, thereby showing also that the indicator behaves as if it were a single acid or base.

---

[1] In this equation K_W is the ionization-constant of water, γ_B the ionization of the free NaOH, and C the concentration and γ the ionization of the salt in the solution.

[2] The contrary opinion expressed by Acree (*Am. Chem. J.*, 38, 35 (1907)) and his conclusion that the mass-action law would permit salts of tautomeric acids to exhibit "abnormal hydrolysis," even though equilibrium has been attained, seems to the writer clearly erroneous.

A satisfactory indicator must also fulfil the following conditions:

(*d*) The conversion of one tautomeric form into the other must take place almost instantaneously, for otherwise equilibrium will not be attained under the conditions of the titration.

(*e*) The color-change must be wholly due to the conversion of one tautomeric form into another; and it must moreover be determined only by the hydrogen-ion concentration, and not to an important extent by any other factor that may be involved, such as the presence of neutral salts in the solution.[1]

It is only to indicators which substantially fulfil these conditions that the principles presented in the following pages apply; and it is an important experimental problem to determine to what extent each special indicator conforms to these requirements.

3. *Equilibrium Relations of Indicators with Reference to the End-Point of Titrations.*—The end-point of a titration may be described as the condition attained when such quantities of base BOH and acid HA have been mixed that, as shown by the color-change, a definite fraction α of the indicator acid HIn is transformed into its salt BIn, or a definite fraction α of the salt InA of the indicator base is transformed into the free base InOH, the indicator transformation being for the sake of definiteness considered always to have taken place in the direction from acid to alkaline, in whichever direction the titration may actually have been made. For the ratio of the untransformed to the transformed fraction we then have, when the indicator is an acid,

$$\frac{1-\alpha}{\alpha} = \frac{(\mathrm{HIn})}{(\mathrm{In}^-) + (\mathrm{BIn})} = \frac{(\mathrm{HIn})}{(\mathrm{In}^-)/\gamma}, \qquad (6)$$

where γ represents the ionization of the indicator salt, which can be regarded as equal to the average value for other salts of the same (uni-univalent) type.

The ratio of the untransformed to the transformed fraction, when the indicator is a base, is:

---

[1] Thus Michaelis and Rona (*Z. Elektrochem.*, 14, 251 (1908)) have shown that the color of Congo red is greatly influenced by neutral salts, especially by those with bivalent and trivalent metallic elements, owing to coagulation of the particles of the indicator. They also state that the colors of methyl violet and (to a less extent) of methyl orange and phenolphthalein are similarly affected by neutral salts, though it is not shown that the effect is here due to the same cause. Several investigators have shown also that a small proportion of alcohol has a relatively large effect in discharging the color of phenolphthalein (cf. Hillebrand, THIS JOURNAL, 30, 1914 (1908)). The researches of Acree (*Am. Chem. J.*, 39, 528 (1908)) and Wegscheider (*Z. Elektrochem.*, 18, 510 (1908)) upon phenolphthalein have shown, moreover, that the behavior of an indicator may be complicated by its acting as a dibasic acid (thus making possible its existence in any of the six forms $\mathrm{H_2In}$, $\mathrm{H_2In'}$, $\mathrm{HIn^-}$, $\mathrm{HIn'^-}$, $\mathrm{In^=}$, and $\mathrm{In'^=}$).

$$\frac{1-\alpha}{\alpha} = \frac{(\mathrm{In}^+) + (\mathrm{InA})}{(\mathrm{InOH})} = \frac{(\mathrm{In}^+)/\gamma}{(\mathrm{InOH})}. \tag{7}$$

We may eliminate from each of these equations the concentration-ratio in the last member by combining with it the first or second of the following ionization equations, which correspond to equations (4) and (5) considered in the last section:

$$\frac{(\mathrm{H}^+)(\mathrm{In}^-)}{(\mathrm{HIn})} = K_{\mathrm{IA}}. \tag{8}$$

$$\frac{(\mathrm{OH}^-)(\mathrm{In}^+)}{(\mathrm{InOH})} = K_{\mathrm{IB}}. \tag{9}$$

The combination of these equations with (6) and (7) evidently leads to the following results:

$$(\mathrm{H}^+) = \frac{(1-\alpha)K_{\mathrm{IA}}}{\alpha\gamma}; \text{ and} \tag{10}$$

$$(\mathrm{OH}^-) = \frac{\alpha K_{\mathrm{IB}}}{(1-\alpha)\gamma}. \tag{11}$$

If in the last equation we substitute for (OH^-) the value of it given by the mass-action equation expressing the ionization of water,

$$(\mathrm{H}^+)(\mathrm{OH}^-) = K_{\mathrm{W}}, \tag{12}$$

we get the following expression:

$$(\mathrm{H}^+) = \frac{(1-\alpha)\gamma K_{\mathrm{W}}}{\alpha K_{\mathrm{IB}}} \tag{13}$$

Equations (10) and (13) are the fundamental equations upon which the theory of indicators is based. They express the principle that in any titration with a given indicator *the end-point* (determined so as to correspond to a definite color-change) *is reached when the hydrogen-ion concentration in the titrated solution attains a definite value,* and that the end-point is determined solely by that concentration. This definite value varies, however, with the ionization-constant of the indicator, and with the proportion of the indicator transformed.[1]

---

[1] It follows from this principle that the ionization-constant of an indicator can be determined, as has been done by Friedenthal, Salessky, Fels, and Salm, by adding it to a series of solutions of decreasing hydrogen-ion concentration until the color-change shows that a definite fraction of it has been transformed. Conversely, the unknown hydrogen-ion concentration in any solution (for example, in that of a very weak acid or hydrolyzed salt) can be determined by adding to it a series of indicators of decreasing ionization-constants—a principle previously applied by Salm and others. This principle may be expected, on account of the ease with which the experiments can be made, to have many important technical applications, especially in cases where a small degree of acidity or alkalinity is to be approximately determined. In place of a series of indicators, the use of a single indicator (2,5-dinitrohydroquinone) which shows a series of markedly different colors in solutions varying in hydrogen-ion concentration by powers of 100 from 10^{-2} to 10^{-12} has recently been proposed by Hender-

It is evident from a comparison of equations (10) and (13), since the value of (H^+) determines the end-point, that a basic indicator of ionization-constant K_{IB} behaves exactly as if it were an acid indicator having an ionization-constant K_{IA} equal to $\gamma^2 K_W/K_{IB}$. Although it is for this reason impossible to determine from its behavior upon titration whether a given indicator is an acid or base, yet for practical purposes all that is essential to know about a basic indicator is the value of the constant, which an acid indicator would have that showed a behavior identical with that of the basic indicator in question.

Mention may finally be made of the fact that the ratios K_{IA}/γ and K_{IB}/γ that occur in equations (10) and (13) are equal to the ionization-constants that would be calculated if, disregarding the degree of ionization of the indicator salt, the color due to the latter were taken as a measure of the concentration of the indicator ion. That this is so becomes obvious upon dividing both members of equations (8) and (9) by γ. For the ratio K_{IA}/γ and for the ratio $\gamma K_W/K_{IB}$ will hereafter be written simply K_I, and this will be called the *apparent ionization-constant* of the indicator.

4. *Experiments Illustrating the Relation between the Color-Change of Indicators and the Hydrogen-Ion Concentration.*—The fundamental principle of the theory of indicators and the fact that the various indicators change color at different hydrogen-ion concentrations may be illustrated by the following experiments, which are described in a form adapted to lecture demonstration.[1]

Prepare one liter of each of nine solutions, whose hydrogen ion concentration differs progressively by each power of 10 from 10^{-3} normal to 10^{-11} normal by proceeding as follows:

(H^+) = 10^{-3} to 10^{-5}: Make up for use in preparing these solutions 3 liters of 0.1 normal acetic acid (concentration to be accurate within 5 per cent.) by dissolving 18.0 g. glacial acetic acid in 3000 cc. distilled water.

(H^+) = 10^{-3}: Mix 570 cc. 0.1 normal acetic acid solution with 430 cc. water, yielding a 0.057 normal solution of the acid. For this case:

$(H^+)(Ac^-) = (H^+)^2 = K_A(HAc) = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-2})$; therefore $(H^+) = 10^{-3}$.

(H^+) = 10^{-4}: Dissolve 0.020 formula wt. sodium acetate, equal to 2.7 g. $NaC_2H_3O_2.3H_2O$, in one liter of 0.1 normal acetic acid. In this case:

$$(H^+) = K_A \frac{(HAc)}{(Ac)} = (1.8 \times 10^{-5}) \frac{10^{-1}}{0.9 \times 2.0 \times 10^{-2}} = 10^{-4}.$$

(The 0.9 in the denominator represents the ionization of the sodium acetate.)

---

son and Forbes (THIS JOURNAL, 32, 687 (1910)). Attention may in passing also be called to the fact that for the case that $\alpha = 1/2$, that is, that the indicator is half transformed, equations (10) and (13) assume the simple forms:

$$(H^+) = K_{IA}/\gamma \text{ and } (H^+) = \gamma K_W/K_{IB}.$$

[1] To Mr. B. H. St. John, who ably assisted me in working out these experiments, I desire to express my indebtedness.

$(H^+) = 10^{-5}$: Dissolve 0.11 formula wt. sodium acetate, equal to 15.0 g. $NaC_2H_3O_2.3H_2O$, in 500 cc. water, and add 500 cc. 0.1 normal acetic acid. In this case:

$$(\mathrm{H}^+) = K_\mathrm{A}\frac{(\mathrm{HAc})}{(\mathrm{Ac})} = (1.8 \times 10^{-5})\frac{5 \times 10^{-2}}{0.8 \times 0.11} = 10^{-5}.$$

$(H^+) = 10^{-6}$ to 10^{-11}. Make up 10 liters of a 0.1 formal[1] solution of $Na_2HPO_4.12H_2O$ by dissolving 358 grams of the crystallized salt in this quantity of water. (As the concentration of this solution should be known within about $^1/_2$ per cent., it is well as a control to evaporate a 100 cc. portion of it in a platinum dish and to ignite and weigh the residue of sodium pyrophosphate.) Prepare also a 0.1 normal solution of hydrochloric acid and one of sodium hydroxide (or some other strong base), and determine their concentrations within 0.3–0.5 per cent. By mixing the phosphate solution in appropriate proportion with the acid or base, we may prepare solutions of the desired hydrogen-ion concentration; for the added acid or base converts the hydrophosphate-ion $(HPO_4^=)$ almost quantitatively into dihydrophosphate-ion $(H_2PO_4^-)$ or into phosphate-ion $(PO_4\ )$; and the ratio which the concentration of these must bear to that of the hydrophosphate-ion in order to give the desired hydrogen-ion concentration can be readily calculated from the ionization-constants (K_2 and K_3) of the second and third hydrogens of phosphoric acid as determined by Abbott and Bray.[2] We have namely the relations:

$$\frac{(\mathrm{H_2PO_4^-})}{(\mathrm{HPO_4^=})} = \frac{(\mathrm{H}^+)}{K_2} = \frac{(\mathrm{H}^+)}{2.0 \times 10^{-7}}, \text{ and } \frac{(\mathrm{PO_4}\ )}{(\mathrm{HPO_4^=})} = \frac{K_3}{(\mathrm{H}^+)} = \frac{3.6 \times 10^{-13}}{(\mathrm{H}^+)}.$$

Substituting the various values of (H^+) we may get the values of the first members of these equations, and from them by a simple transformation the values of the ratios given in the following table:

(H^+)	$\frac{(H_2PO_4^-)}{(H_2PO_4^-) + (HPO_4^=)}$	$\frac{(PO_4\ )}{(PO_4^\equiv) + (HPO_4^=)}$
10^{-6}	0.833 (0.850)	....
10^{-7}	0.333 (0.450)	....
10^{-8}	0.047 (0.050)	....
10^{-9}	0.005 (0.0)	....
10^{-10}	...	0.0036 (0.030)
10^{-11}	...	0.036 (0.140)

(The values within parentheses are those derived by Salm (*Z. physik. Chem.*, **57**, 480 (1907)) by an entirely different method, namely, by determining (H^+) by measuring the electromotive force of hydrogen gas cells containing the phosphate solutions as electrolytes.)

These ratios evidently represent the fraction of the hydrophosphate in the original solution which is to be transformed by the addition of the acid or base. Assuming the latter to have the same formal concentration as the phosphate solution, then the various standards may be made up by mixing the quantities of the solutions shown in the following table:

(H^+).	Na_2HPO_4 solution. cc.	HCl solution. cc.	NaOH solution. cc.
10^{-6}	600	500	..
10^{-7}	700	350	..
10^{-8}	1000	47	..
10^{-9}	1000	5	..
10^{-10}	1000	..	3.6
10^{-11}	1000	..	36

[1] In accordance with the practice of this laboratory, a solution containing x formula weights of solute per liter is designated an x-formal solution.

[2] THIS JOURNAL, 31, 760 (1909).

(The accuracy of the first of these standards is evidently especially sensitive to errors in the relative concentrations of the hydrophosphate and acid solutions, since so large a proportion of the former is converted into dihydrophosphate.)

Arrange 27 lecture jars or large lecture test tubes in three rows of nine, preferably upon a wooden stand covered with white cloth or paper and made in the form of three long narrow steps, so that each row will be visible above or below the other rows. Place 200 cc. of the $(H^+) = 10^{-3}$ solution in each of the jars at the left end of the three rows, 200 cc. of the $(H^+) = 10^{-4}$ solution in the three jars next to these, and so on till all the jars are charged with the nine standard solutions. Place cards with large figures —3, —4, —5, etc., pasted or marked upon them above each set of three jars.

Prepare in small 100 cc. bottles about 100 cc. of the following indicator solutions:

(*a*) 0.5 per cent. solution of thymolphthalein (TP) in alcohol.
(*b*) 0.5 per cent. solution of phenolphthalein (PP) in alcohol.
(*c*) 0.5 per cent. solution of rosolic acid (RA) in 50 per cent. alcohol.
(*d*) 0.1 per cent. solution of methyl red[1] (MR) in water.
(*e*) extract of cochineal (Coc) commonly employed in volumetric analysis.
(*f*) 0.1 per cent. solution of methyl orange (MO) in water.

Place in each of these indicator solutions a straight tube about 15 cm. long and 8 mm. in bore slightly constricted at its lower end.

When the demonstration is to be made, add by means of the straight tubes, capped temporarily with the finger, about 2 cc. of the appropriate indicator solutions to the various jars in the manner shown in the following table, where the letters represent the indicators to be added:

10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}
...	MR	MR	MR*	MR	TP	TP	TP	TP*
Coc	Coc	Coc*	Coc	...	PP	PP*	PP	PP
MO	MO*	MO	RA	RA*	RA	RA	...	...

The stars in the above table show the point at which the transition-color of the indicator is most marked.

5. *Discussion of the Indicator-Function.*—In the following discussion we will for the sake of brevity substitute for the cumbrous expressions for (H^+) given in equations (10) and (13) a single letter k. That is, we will put:

$$k = \frac{(1-\alpha)K_{IA}}{\alpha\gamma} = \frac{(1-\alpha)\gamma K_w}{\alpha K_{IB}} = \frac{1-\alpha}{\alpha}K_I. \qquad (14)$$

It is evident that k is a quantity that depends on the apparent ionization-constant of the indicator and on the proportion of it transformed in the titration. For brevity it will throughout this article be designated the *indicator-function.*[2]

---

[1] A new, apparently very satisfactory indicator recently described by Rupp and Loose (*Ber.*, 41, 3905 (1908)) and readily prepared according to their directions. See also *C. A.*, 3, 523 (1909).

[2] In consequence of some complication, such, for example, as would arise if the indicator were a dibasic acid or if neutral salts influenced its ionization relations or its tautomeric equilibrium, the hydrogen-ion concentration may be some other function of the fraction transformed than that expressed by equations (10) and (13). In that case the true functional relation $(H^+) = f(\alpha)$ might be determined by experiment; and

The function k plays a most important part throughout the following considerations; and it will be seen later that when the titration is sensitive to errors, its accuracy is determined by the closeness with which a definite value of k can be realized. It is therefore well to consider in advance the practical conditions regulating the values of the two factors α and K_I which determine k and their bearing on the quantity of indicator that should be employed. It is evident that theoretically any desired value of k could be secured with any indicator of any ionization-constant K_I by giving α, the fraction of it transformed at the end-point, an appropriate value. To secure accuracy, however, α must be given (1) such a value that the eye can best recognize a small percentage change in its value, and (2) such a value that k will not be unnecessarily sensitive to the unavoidable error in so determining the end-point as to give the desired value of α.

The second of these conditions, which can be treated very simply in a mathematical way, may be first considered. By differentiating equation (14), and dividing the result by the original equation, we get:

$$\frac{dk}{k} = \frac{dK_I}{K_I} - \frac{d\alpha}{\alpha(1-\alpha)}$$

This equation shows that any small fractional error in α (represented by $d\alpha/\alpha$) causes a fractional error in k (represented by dk/k) which is $1/(1-\alpha)$ times as large as that in α. The quantity $1/(1-\alpha)$, however, evidently approaches a minimum value of unity as α approaches zero. Yet, it is to be noted that $1/(1-\alpha)$ does not change very greatly until α assumes a fairly large value; thus for $\alpha = 25\%$, $1/(1-\alpha)$ becomes only 1.33; so that any value of α up to say 25 per cent. is nearly as good as a much smaller value, so far as this effect is concerned. The conclusion to be drawn is, therefore, that α should always be given a fairly small value, which may, however, if other conditions require it, be made as large as 25 per cent.

If the indicator is being transformed in the other direction, by the addition of an acid rather than a base, and the color-change being observed is that corresponding to the form of the indicator whose proportion is represented by $(1-\alpha)$, it also is true that the fraction of it *so* transformed must be relatively small. For the last term of the preceding equation can be written $+\frac{1}{\alpha}\frac{d(1-\alpha)}{1-\alpha}$, from which it is evident that the multiplying factor $1/\alpha$ approaches a minimum value of unity as α approaches unity.

if k were then understood to signify the value of that function in any given case, all the formulas derived in the following sections of this article would still be valid; for in the derivation of them k merely represents the value which (H^+) has at the end-point of the titration.

The other condition—that relating to the sensitiveness of the eye to the color-change—may be first considered for the case of one-color indicators, such as phenolphthalein, paranitrophenol, or cyanine, which are colorless in acid and colored in alkaline solution. Evidently in this case the definite depth of color, to a change in which the eye is most sensitive, may be attained by varying either the total concentration of the indicator (ΣIn) or the fraction (α) of it transformed, for the depth of color is proportional to the product $\alpha(\Sigma\text{In})$. Therefore by adding different quantities of indicator we can often vary α within fairly wide limits without sacrificing sensitiveness, and thereby attain even with a single indicator of constant K_I a fairly large variation in the value of k. Thus when the indicator is sufficiently soluble, it might well be practicable to vary α from 0.1 per cent. to 25 per cent.[1] which would correspond to a variation of k from 1000 K_I to $3K_I$. A minimum value for α is, however, often determined by the fact that the solubility of the indicator in water is not sufficient to allow the necessary depth of color to be secured without increasing α beyond that minimum value.[2] Thus, if I represents the value of the concentration α (ΣIn) of the transformed part of the indicator which gives the proper intensity of color, and if S is the solubility of the indicator (that is, the value of the concentration (ΣIn) in the saturated solution), the relation $\alpha > I/S$, and therefore also the relation $k < \frac{S - I}{I} K_I$, must evidently hold true.

In the case of a one-color indicator, the relation between depth of color, concentration of indicator, and fraction transformed can be experimentally determined by placing a measured quantity (1 to 5 cc.) of its solution in a graduate, adding 5 to 10 cc. of 0.1 normal alkali solution (whereby the indicator will be completely transformed) and enough water to make the volume 100 cc., and then diluting measured fractional portions (say 10 cc. and 1 cc.) of this solution to 100 cc. The resulting color corresponds to that which the quantity of indicator taken at the start gives to 100 cc. liquid when the fraction of it transformed equals the fraction ($^1/_{10}$ and $^1/_{100}$) of the solution that was diluted. In this way the quantity of indicator that must be added to secure any desired fractional transformation and at the same time the desired depth of color can readily be determined.

---

[1] The upper value of α here mentioned is so chosen as to accord with the considerations of the preceding paragraphs. The lower value, though not necessarily the limit in all cases, could hardly ever be much further reduced without adding an extraordinary amount of the indicator.

For example, experiments that have been made with p-nitrophenol in the way described in the next paragraph show that, if 10 cc. of its saturated solution in water were added to 100 cc. of water, a depth of color sufficient to constitute a satisfactory end-point would be obtained by transforming 0.1 per cent of the indicator into its salt.

[2] For example, experiments made with phenolphthalein have shown that when the solution to be titrated is saturated with it, about 4 per cent. of it must be transformed into its salt to give such a depth of color as would serve as a satisfactory end-point. This minimum value of α corresponds to a maximum value of k equal to 24 K_I. In the case of thymolphthalein, on the other hand, it was found that in an aqueous solution saturated with it a suitable color is obtained only when about $^1/_2$ of the indicator is transformed into its salt.

In the case of two-color indicators, such as methyl orange, dimethylaminoazobenzene, methyl red, cochineal, and rosolic acid, the fraction transformed can not be similarly varied without a great sacrifice of sensitiveness; for, owing to the fact that the indicator has a color in the untransformed state, the fraction transformed must have a considerable value in order that its own color may be visible. What the best fraction to have transformed is, depends on the character and intensity of the two colors which the indicator exhibits; but ordinarily it is probably between 5 and 20 per cent.[1] The value of k practically attainable with a two-color indicator which is being transformed by passing from the acid to alkaline condition and which has an ionization-constant K_I is therefore ordinarily in the neighborhood of 10 K_I. On the other hand, if the color-change be determined in passing from the alkaline to the acid condition, and if say 9 per cent. of the indicator be transformed in this direction at the end-point (in which case $1 - \alpha = 0.09$ and $\alpha = 0.91$), the value of k becomes $^1/_{10}K_I$.

While a two-color indicator does not possess the same graded adaptability that a one-color indicator possesses, yet it will be seen from the illustration just given that the color-changes at both limits of its transformation may be utilized, provided the eye is sufficiently sensitive to both these changes.

In the case of a two-color indicator, the relation between color-change and fraction transformed can be experimentally studied by preparing a solution of the indicator of any appropriate concentration, dividing this into two parts, adding a small quantity of hydrochloric acid to one part and of sodium hydroxide to the other so as to transform it completely in one direction or the other, then superposing in suitable tubes or beakers a layer of one of these solutions above a layer of the other, and looking through the two layers. The relative thickness of the two layers, or the concentration of the one or the other solution, may then be varied, and the colors compared.

Summing up these considerations we may therefore say that we can in general secure, in the case of one-color indicators (by using a suitably adjusted quantity of the indicator), and in the case of two-color indicators (by titrating in the one direction or the other), values of the indicator-function k which are given by the following expressions, in which K_I is the apparent ionization-constant of the indicator:

---

[1] Experiments made by me with methyl orange have shown that a satisfactory change of color in the direction from yellow to orange is secured when from 5–20 per cent. (depending on the concentration) is transformed, but that in the direction from pink to orange from 20–30 per cent. must be transformed.

$k > 3K_\mathrm{I}$ and $< \frac{S - I}{I} K_\mathrm{I}$ for one-color indicators of limited solubility S. (15*a*)

$k > 3K_\mathrm{I}$ and $< 1000\, K_\mathrm{I}$, for one-color indicators of sufficient solubility. (15*b*)

$k =$ approx. $10\, K_\mathrm{I}$ or $=$ approx. $^1/_{10}\, K_\mathrm{I}$, for two-color indicators. (16)

It is to be understood, however, that these are only rough general estimates. It is therefore desirable to emphasize the importance of supplementing in any investigation of specific indicators the determination of their ionization-constants by an experimental study of the absolute concentration (I) which the colored form of the indicator must have in order to give a satisfactory color-intensity, of its solubility in water, and of the limits between which it is practicable to vary the fraction of it transformed. Only in this way will an exact application of the theory of indicators to volumetric analysis be made possible.

6. *Concentration of the Indicator.*—Besides these limitations in regard to the fraction of the indicator transformed, there is for an entirely different reason a maximum limit placed on the total normal concentration (ΣIn) of the indicator. Namely, it is evident that the concentration of the indicator salt in the solution titrated to the end-point must in general be negligibly small in comparison with the molal concentration (C) of the salt produced by the neutralization of the base BOH and the acid HA; since otherwise an appreciable excess of the base BOH, if the indicator is an acid, or of the acid HA if the indicator is a base, will be used up in combining with the indicator. Since the fraction of the indicator existing as its salt is α if the indicator is an acid, and is $1 - \alpha$ if the indicator is a base, this condition in regard to the concentration of the indicator may be expressed as follows, if we represent by ρ the maximum fractional error that is considered permissible in the titration:

$$(\Sigma\mathrm{In}) < \frac{\rho C}{\alpha} \text{ for an acid indicator.} \qquad (17)$$

$$(\Sigma\mathrm{In}) < \frac{\rho C}{1 - \alpha} \text{ for a basic indicator.} \qquad (18)$$

By these expressions the maximum quantity of indicator that may be added to a given volume of solution in any titration without introducing a fractional error greater than ρ may readily be calculated.[1]

---

[1] Thus if an accuracy of 0.1 per cent. ($\rho = 10^{-3}$) is desired, if the indicator is an acid and the fraction of it transformed at the end-point is 10 per cent. ($\alpha = 10^{-1}$), and if the concentration of the salt in the titrated solution is 0.05 normal ($C = 5 \times 10^{-2}$),

II. Titration of Monobasic Acids and Monacidic Bases.

7. *General Formulation of the Theory.*—We may now proceed to the solution of our main problem, which consists primarily in deriving expressions for the difference between the quantity of the acid HA and that of the base BOH which have to be brought together in order that the end-point may be reached, confining ourselves in the first instance to the case where the acid is monobasic and the base monacidic. A general solution of this problem involves the treatment of combinations involving any acid of ionization-constant K_A, any base of ionization constant K_B, and any value of the indicator-function k.

The ionization-constants of the acid and base are expressed by the equations:

$$(B^+)(OH^-) = K_B(BOH). \qquad (19)$$

$$(H^+)(A^-) = K_A(HA). \qquad (20)$$

The ionization-constant of water (K_w) is also involved in the subsequent considerations, since it furnishes a relation between the concentrations (H^+) and (OH^-). It is expressed by equation (12) given above. Replacing (H^+) in this equation by k we get:

$$(OH^-) = K_w/k. \qquad (21)$$

It is to be noted that K_w has an extremely small value; namely, about 10^{-15} at 0°, 10^{-14} at 25°, 10^{-13} at 65°, and 5×10^{-18} at 100°.[1]

Let now the total concentration of the acid-constituent A in the solution titrated to the end-point be (ΣA) and that of the base-constituent B in that solution be (ΣB).[2]

---

the concentration of the indicator must be less than 5×10^{-4} normal or 1/2000 normal; and if the volume of the titrated solution is 100 cc., less than 1/20,000 of a formula weight of indicator must be added to it.

That the concentration of the indicator is in practice ordinarily less than 1/2000 normal will be seen from the following facts: Solutions of indicators are usually prepared so as to contain 1 to 5 grams of the indicator per liter. This latter value corresponds to 0.016 of a formula weight per liter (assuming the average formula weight to be 300). Of such solutions less than 1.0 cc. is commonly added to say 80 cc. of the titrated solution. This makes the concentration of the indicator in the latter less than 0.0002 formal.

[1] The values of this constant at 0 and 25° given by Kanolt (THIS JOURNAL, **29**, 1414 (1907)) are somewhat lower, namely, 0.88×10^{-15} at 0° and 0.81×10^{-14} at 25°. Other investigators have, however, found higher values; thus Heydweiller (*Ann. Phys.*, [4] **28**, 512 (1909)) through a recalculation of the experiments made by him and Kohlrausch obtained 1.16×10^{-15} at 0° and 1.04×10^{-14} at 25° and Lundén (*Meddel. fr. k. sv. vet. Nobelinstitut*, Vol. 1, No. 8, p. 16 (1907)) found 1.05×10^{-14} at the latter temperature. Whatever may be the correct result, the round values are sufficiently accurate for the purposes of this investigation.

[2] The products obtained by multiplying these concentrations by the volume of the titrated solution represent evidently the quantities of the acid HA and base BOH which have been mixed in order to reach the end-point; and the ratio of these concentrations to each other represents the ratio of the said quantities to each other (provided no salt of the acid or base was originally present in either solution).

The different forms in which these two constituents exist in the solution are shown by the following equations which sum up the concentrations of those various forms:

$$(\Sigma B) = (B^+) + (BOH) + (BA). \qquad (22)$$

$$(\Sigma A) = (A^-) + (HA) + (BA). \qquad (23)$$

We have also a further relation expressing the equality of the sums of the concentrations of all the positive and of all the negative ions in the solution, as follows:

$$(B^+) + (H^+) = (A^-) + (OH^-). \qquad (24)$$

It is to be noted that the quantities (H^+) and (OH^-) in a titrated solution are always small in comparison with the quantities (B^+) and (A^-). It is not, however, permissible to cancel them from this equation, since the difference $(B^+) - (A^-)$ is involved in the following derivation. In cases, however, where the value of (B^+) or (A^-) itself, and not their difference, is involved, no serious error will be made by assuming that (B^+) and (A^-) are equal.

8. *The Error in the Titration.*—In order to obtain an expression for the fractional error in the titration we may proceed as follows. We first subtract equation (23) from (22), whereby we obtain:

$$(\Sigma B) - (\Sigma A) = (B^+) - (A^-) + (BOH) - (HA). \qquad (25)$$

We then substitute in this equation the value of $(B^+) - (A^-)$ given by equation (24), whereby we get:

$$(\Sigma B) - (\Sigma A) = (BOH) - (HA) + (OH^-) - (H^+). \qquad (26)$$

Substituting the values of (BOH) and (HA) given by equations (19) and (20), we get:

$$(\Sigma B) - (\Sigma A) = \frac{(B^+)(OH^-)}{K_B} - \frac{(H^+)(A^-)}{K_A} + (OH^-) - (H^+).$$

Replacing in this equation (H^+) by k and (OH^-) by K_w/k, and putting $(B^+) = (A^-)$, which as stated above is justifiable so long as the difference between them is not involved, we get:

$$\frac{\Sigma B - \Sigma A}{(B^+) \text{ or } (A^-)} = \frac{K_w}{kK_B} - \frac{k}{K_A} + \frac{K_w}{k(B^+)} - \frac{k}{(A^-)}. \qquad (27)$$

For the quantity (B^+) or (A^-) in equation (27) expressions in terms of (ΣB) or (ΣA) may be obtained from equations (22) and (23) by substituting for (BOH) and (HA) the same values that were introduced into equation (26) and by substituting for $(BA)/(B^+)$ the quantity $(1 - \gamma)/\gamma$, where γ evidently represents the ionization of the salt BA in the titrated solution. The so-obtained expressions for (B^+) and for (A^-) are:

$$(B^+) = \frac{(\Sigma B)}{\frac{1}{\gamma} + \frac{K_W}{kK_B}} \quad (28); \qquad \text{and } (A^-) = \frac{(\Sigma A)}{\frac{1}{\gamma} + \frac{k}{K_A}}. \quad (29)$$

By introducing these values into equation (27), an exact expression applicable to any combination of base and acid can be obtained.

The practically important cases are, however, those in which either the base or the acid is largely ionized, since such a base or acid is almost invariably employed as a standard solution in the titration. It is therefore worthy of note that in the expression for (B^+) the last term in the denominator, which is equal to the concentration ratio $(BOH)/(B^+)$, is negligible in comparison with the first term when K_B is even moderately large; and that in the expression for (A^-) the last term in the denominator, which is equal to the concentration-ratio $(HA)/(A^-)$, is negligible when K_A is even moderately large.[1] Taking into account these facts, we may write equation (27) in the following substantially exact form, applicable according as (ΣB) or (ΣA) is written in the denominator to the case where the base or the acid is largely ionized:

$$\frac{(\Sigma B) - (\Sigma A)}{(\Sigma B) \text{ or } (\Sigma A)} = \gamma\left(\frac{K_W}{kK_B} - \frac{k}{K_A} + \frac{K_W}{k\gamma(\Sigma B)} - \frac{k}{\gamma(\Sigma A)}\right). \quad (30)$$

This equation also gives approximate results, which are, however, sufficiently accurate for almost all purposes, when applied to the case in which the base and acid are both slightly ionized; for the error in this case is only that arising from neglecting the last term in the denominator of (28) or (29), and this will not give rise to an error in the first member of (30) of more than 1 or 2 per cent. for any combination for which even a very rough titration is possible. Equation (30) will therefore serve as a general basis for the following discussion of the accuracy of the titration and of the conditions determining it.

It will be noted that the first member, which expresses the difference between the concentrations of the basic and acid radicals divided by the concentration of the one or other of these, really represents the fractional error (FE) in the titration in the common case in which the acid and base titrated against each other are the only source of those radicals. That error can therefore be calculated for any combination of indicator, acid, and base by equation (30) or still better by the following, more perspicuous equation,[2] which is obtained from it by a simple transformation and by the substitution of C, representing the normal concentration of the salt in the titrated solution, for (ΣB) and for (ΣA), which are obviously approximately equal to it and to each other so long as FE is even moderately small.

---

[1] Thus, if K_W/k in (28) or k in (29) has a value even as large as 10^{-4}, the last term will be entirely negligible when K_B or $K_A > 10^{-2}$. For the strongest bases like potassium hydroxide or the strongest acids like hydrochloric or nitric acid, the value of K_B or K_A at 0.1 normal is about 1, while for barium hydroxide it is about 0.3 and for the second hydrogen of sulphuric acid about 0.03.

[2] Consider, for example, the case where 0.1 normal ammonium hydroxide is titrated at 25° with 0.1 normal hydrochloric acid, using phenolphthalein as an indica-

$$\overline{\text{FE}} = \frac{\gamma K_w}{k K_B}(1 + K_B/\gamma C) - \frac{\gamma k}{K_A}(1 + K_A/\gamma C). \qquad (31)$$

Of the quantities occurring in this equation it is to be noted that the ionization γ has nearly the same value at the same concentration for all salts of monobasic acids and monacidic bases, the average value for uniunivalent salts at various concentrations at 20° being approximately as follows:

Normal concentration.	0.50	0.20	0.10	0.05	0.02	0.01
Ionization (γ).	0.70	0.78	0.83	0.86	0.91	0.93

If the intermediate value 0.80 be employed, the result will be sufficiently accurate in almost all cases.

It may also be mentioned that all of the most completely ionized monacidic bases and monobasic acids (such as sodium and potassium hydroxides and hydrochloric and nitric acids) have an ionization at room temperature in 0.1 normal solution which corresponds to a ionization-constant of about unity.[1] The corresponding values of the parentheses $(1 + K_B/\gamma C)$ or $(1 + K_A/\gamma C)$ when K_B or $K_A = 1$ are 24 for $C = 0.05$, and 4.0 for $C = 0.5$. These are evidently the maximum values for these parentheses, since their values approach unity as K_B or K_A decreases.

9. *Error in the Titration when a Neutral Salt is Originally Present.*—Equation (30) is also applicable to the not uncommon case in which there

---

tor (for which $K_I = 2 \times 10^{-10}$), the indicator being at the end-point 10 per cent. transformed. In this case:

$$k = \frac{K_I(1 - \alpha)}{\alpha} = \frac{2 \times 10^{-10} \times 0.90}{0.10} = 2 \times 10^{-9};\ \gamma = 0.86;\ C = 0.05;\ K_A = 1;$$

and $K_B = 1.8 \times 10^{-5}$.

Substituting the appropriate numerical values in equation (31) we get:

$$\overline{\text{FE}} = \frac{0.86 \times 10^{-14} \times 1}{(2 \times 10^{-9})(1.8 \times 10^{-5})} - \frac{0.86(2 \times 10^{-9})(1 + 1/0.043)}{1.0} = 0.24 = 24\%.$$

That is to say, an error of 24 per cent. will be made in the titration.

Suppose now that the same titration be made, using p-nitrophenol as indicator (for which $K_I = 9 \times 10^{-8}$), and causing it to be one per cent. transformed. Equation (31) then becomes:

$$\overline{\text{FE}} = \frac{0.86 \times 10^{-14} \times 1}{(9 \times 10^{-6})(1.8 \times 10^{-5})} - \frac{0.86(9 \times 10^{-6})(1 + 1/0.043)}{1.0} = 0.0005 = 0.05\%.$$

[1] The constant unity corresponds to an ionization-value 0.916 at 0.1 normal, while the ionization values at 18° derived from the conductivity measurements made in this laboratory are 0.926 for HCl, 0.918 for HNO_3, 0.902 for NaOH. Even if, as suggested by Noyes and Kato (THIS JOURNAL, 30, 334 (1908)), the ionization of these acids is as small as that of potassium chloride (86.0 per cent. at 0.1 normal), the ionization-constant would be of the same general magnitude; namely, 0.53 instead of 1.0.

is present in the original solution, together with the acid HA or base BOH which is to be titrated, some of the neutral salt BA. This is true since this equation expresses the equilibrium conditions prevailing in the solution in which the end-point has been reached, and since it evidently makes no difference whether all of the salt was produced by the titration or whether some of it was originally present. It is evident, however, that in the latter case equation (30) does not express the fractional error in the titration of the free acid or base, since the difference between the concentrations of the basic and acid constituents must then be referred, not to the total concentration (ΣB) or (ΣA) of either of them, which is substantially equal to the concentration C of the salt in the titrated solution, but to the concentration $C - C_0$ which has been produced in that solution through the addition of the standard base or acid (C_0 therefore corresponding to the quantity of salt originally present). We have therefore for the fractional error FE′ in the titration in this case:

$$\mathrm{FE}' = \frac{(\Sigma \mathrm{B}) - (\Sigma \mathrm{A})}{C - C_0} = \left(\frac{(\Sigma \mathrm{B}) \text{ or } (\Sigma \mathrm{A})}{C - C_0}\right)\left(\frac{(\Sigma \mathrm{B}) - (\Sigma \mathrm{A})}{(\Sigma \mathrm{B}) \text{ or } (\Sigma \mathrm{A})}\right),$$

$$\text{or } \mathrm{FE}' = \frac{C}{C - C_0}\,\mathrm{FE}, \qquad (32)$$

the value of the last parenthesis or of FE being that expressed by equation (30) or (31).

The fractional error in the case where a neutral salt of the acid and base involved in the titration is originally present is therefore greater in the proportion which the sum of the quantity of that salt and of the quantity of acid or base used in the titration bears to the latter quantity.

It can furthermore be shown, by formulating the condition equations as in section 7, that the fractional error in the titration can be correctly calculated by equation (32) also in the following cases:

(*a*) When a not largely ionized acid HA is titrated with a largely ionized base BOH, and a neutral salt B′A of another largely ionized base B′OH is originally present.

(*b*) When a not largely ionized base BOH is titrated with a largely ionized acid HA, and a neutral salt BA′ of another largely ionized acid HA′ is originally present.

10. *The Best Value of the Indicator-Function.*—Equation (31) may be employed to determine what the value of the indicator-function is which will give the best result in titrating an acid of known ionization-constant K_A with a base of known ionization-constant K_B, when the titrated solution has a given concentration C. To determine this, we need only place FE equal to zero and solve for k. We thus obtain the following expression, in which this "best value" of k is represented by k_0:

$$k_0 = \left(\frac{K_W(1 + K_B/\gamma C)}{K_B}\right)^{\frac{1}{2}} \left(\frac{K_A}{1 + K_A/\gamma C}\right)^{\frac{1}{2}} = \sqrt{\left(\frac{K_WK_A}{K_B}\right)\left(\frac{1 + K_B/\gamma C}{1 + K_A/\gamma C}\right)}. \qquad (33)$$

It is evident from equation (33) that the best value of the indicator-function is equal to the square-root of the ionization-constant of water when the ionization-constants of the base and acid are equal, and that it is smaller than this when the acid is slightly ionized and larger when the base is slightly ionized. The best value can, of course, be exactly calculated for any given case.[1]

11. *Limiting Values of the Indicator-Function.*—It is evident from equation (33) that for any combination of acid or base whatever there is a value of the indicator-function which would theoretically make possible an exact titration. Yet it is a well-known fact that, if either the acid or base has too small an ionization-constant, accurate results can not in practice be obtained. This arises from the impossibility of realizing in the titration a value of the indicator-function identical with the best value, and from the sensitiveness of the titration in certain cases to the deviation of the actual value k from the best value k_0. What the realization of the desired value of the indicator-function involves will be seen by considering the following expression for the ratio k_0/k, which may be obtained by combining equations (33) and (14):

$$\frac{k_0}{k} = \frac{(K_WK_A/K_B)^{\frac{1}{2}}}{K_I(1 - \alpha)/\alpha}\left(\frac{1 + K_B/\gamma C}{1 + K_A/\gamma C}\right)^{\frac{1}{2}}. \qquad (34)$$

In order to make this expression as nearly as possible equal to zero, one would in practice first select an indicator with such an ionization-constant K_I that k_0/k can become zero when a practicable fraction of the indicator is transformed, then would calculate by (34) just what the fraction transformed α should be to make k_0/k equal to unity, and finally would attempt to realize in the titration this fraction transformed by comparison with a standard color so prepared as to correspond to it (see Section 5). It will be seen that there are two errors involved in this process; first, the error in the calculation of α arising from the errors in the assumed values of the various ionization-constants, of which errors that in K_I is likely with our present knowledge to be the largest; and second, the error in the experimental determination of α arising from the failure to titrate to the depth or shade of color which corresponds to the proper fraction transformed. For these reasons the ratio k_0/k will inevitably vary from

---

[1] For example, suppose NH_4OH ($K_B = 1.8 \times 10^{-5}$) is to be titrated at 25° ($K_W = 10^{-14}$) with HCl ($K_A = 1$), the titrated solution of the salt being 0.05 normal ($C = 0.05$) and its ionization γ being 0.86. We then have:

$$k_0^2 = \frac{10^{-14} \times 1}{1.8 \times 10^{-5}} \times \frac{1}{24}; \text{ whence } k_0 = 4.8 \times 10^{-6}.$$

unity by a considerable amount; and it is therefore important to consider the conditions which determine the sensitiveness of the titration to this variation.

The practical problem may be concretely stated as follows: to determine how much the actual value of the indicator-function k may vary from the best value k_0 without causing a fractional error $\overline{FE}$ in the titration greater than the accuracy which is aimed at. To solve this problem we may multiply each of the terms of the second member of equation (31) by k_0/k_0, substitute in the denominator of the first and in the numerator of the second term the value of k_0 given by equation (33), and transform, whereby we get:

$$\overline{FE} = \gamma\left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{K_W}{K_A K_B}\right)^{\frac{1}{2}}\left(1 + \frac{K_B}{\gamma C}\right)^{\frac{1}{2}}\left(1 + \frac{K_A}{\gamma C}\right)^{\frac{1}{2}}. \quad (35)$$

It is obvious that in equation (35) the value of the first parenthesis, which is nearly identical with k_0/k or k/k_0 when this is greater than (say) 3, must evidently for a given value of $\overline{FE}$ be smaller, the larger the values of the other three parentheses. The last two of these do not, however, vary very greatly from unity; thus in the rather extreme case in which K_B or $K_A = 1$ and $C = 0.05$, one or other of these factors has the value 4.9. It is therefore the very variable second factor $(K_w/K_A K_B)^{1/2}$ that mainly determines how large the arithmetical value of k_0/k or k/k_0 may be without causing the fractional error in the titration to exceed any given value. It is evident now that this factor increases as the product $(K_A K_B)$ of the ionization-constants of the acid and base decreases, and assumes a considerable magnitude only when the value of this product approaches that of the ionization-constant of the water. The percentage error in the titration therefore increases under the same conditions.[1]

The maximum value, which k_0/k or k/k_0 may be allowed to assume when a definite fractional accuracy ρ is desired in the titration, may be calculated for various values of $K_w/K_A K_B$, by substituting, in equation (35) for $\overline{FE}$ the given value of ρ and for $K_B/\gamma C$ and $K_A/\gamma C$ in the last two factors, the values which they have in the titration under consideration.

---

[1] Compare, for example, the values of the percentage error ($100\ \overline{FE}$) given in the last column of the following table for various combinations of acids and bases. In the calculations of these quantities by (35) it is assumed that $K_W = 10^{-14}$ as it is at 25°, that $C = 0.05$, that $\gamma = 0.86$, and that k_0/k or $k/k_0 = 5$, which is about as small a value as can be realized in practice without taking unusual precautions.

Acid.	Base.	K_A.	K_B.	$(K_W/K_A K_B)^{\frac{1}{2}}$.	$100\ \overline{FE}$.
HCl	KOH	1	1	10^{-7}	0.001
$HC_2H_3O_2$	KOH	2×10^{-5}	1	2×10^{-5}	0.05
HCl	NH_4OH	1	2×10^{-5}	2×10^{-5}	0.05
HBO_2	KOH	7×10^{-10}	1	4×10^{-3}	9.0
$HC_2H_3O_2$	NH_4OH	2×10^{-5}	2×10^{-5}	5×10^{-3}	2.3

Such a calculation has been made under the assumption that $\rho = 0.1\ \%$ $= 0.001$, for the three following, practically limiting cases:

(1) K_B or $K_A = 1$ and $\gamma C = 0.86 \times 0.05 = 0.043$.

(2) K_B or $K_A = 1$ and $\gamma C = 0.70 \times 0.5 = 0.35$.

(3) $K_B/\gamma C$ and $K_A/\gamma C$ are negligible (less than 0.2).

The results of these calculations are given in the following table, the columns marked (1), (2), and (3) corresponding to the three cases just considered.[1]

TABLE I.—MAXIMUM VALUES OF THE RATIO BETWEEN THE ACTUAL AND BEST VALUES OF THE INDICATOR-FUNCTION FOR AN ACCURACY IN THE TITRATION OF 0.1 PER CENT.

$\frac{K_W}{K_AK_B}$	K_AK_B at 25°.	Maximum value of k_0/k or k/k_0. (1)	(2)	(3)	$\frac{K_W}{K_AK_B}$	K_AK_B at 25°.	Maximum value of k_0/k or k/k_0. (1)	(2)	(3)
10^{-12}	10^{-2}	214	720	..	10^{-7}	10^{-7}	1.44	2.7	4.2
10^{-11}	10^{-3}	74	230	..	10^{-6}	10^{-8}	1.13	1.43	1.8
10^{-10}	10^{-4}	24	73	..	10^{-5}	10^{-9}	1.04	1.12	1.22
10^{-9}	10^{-5}	7.6	23	40	10^{-4}	10^{-10}	1.011	1.04	1.06
10^{-8}	10^{-6}	2.7	7.4	13	10^{-3}	10^{-11}	1.004	1.01	1.02

These maximum values are valid for the case that the accuracy desired is 0.1 per cent. The table will hold true for an accuracy of about 1/3 per cent. if each value of K_w/K_AK_B be multiplied by 10, and it will hold true for an accuracy of 1 per cent. if each value of K_w/K_AK_B be multiplied by 100; and if correspondingly each value of K_AK_B at 25° be divided by 10 or 100.[2]

Attention may also be called to the fact that, since K_w increases rapidly with rising temperature, the maximum value of k_0/k or k/k_0 admissible when a given percentage accuracy is desired is for a given value of K_AK_B larger at lower than at higher temperatures. Thus the values of k_0/k or k/k_0 given in Table I correspond to values of K_AK_B one-tenth as large at 0° and ten times as large at 65° as the values of K_AK_B given in the same row in the table for 25° (since $K_w = 10^{-15}$ at 0° and $= 10^{-13}$ at 65°). Since K_A and K_B for weak acids and bases commonly change with the temperature in a direction opposite to that in which K_w changes (or, since when K_A and K_B change in the same direction they change in a smaller proportion than K_w), it is almost always true that greater accuracy will be secured with any combination of acid, base, and indicator that is sensitive to error by titrating at as low a temperature as possible.[3]

---

[1] In these three cases γ was taken as 0.86, 0.70, and 0.80, respectively.

[2] It will be shown later that this table is also applicable to titrations in which a diacidic base or dibasic acid is involved, provided K_W/K_AK_B be replaced by an appropriate function of the ionization-constants.

[3] Exceptions to this statement may occasionally arise from an entirely different cause—namely, from the fact that the equilibrium of the indicator acid or base with its salt is too slowly established at the lower temperature, owing to a very slow rate of transformation of the two isomeric forms of the indicator into each other.

Certain other practical conclusions that may be drawn from Table 1 and equation (35) may be pointed out. A comparison of columns (1) and (2) shows that the titration is more sensitive to variations in the value of k, the more dilute the solution. It is therefore desirable to titrate in as strong a solution as possible, whenever the conditions are such that an error is likely to arise.

It will also be seen from the table that, as the product K_AK_B decreases in value, greater care must be taken to approximate to the best value of the indicator-function by selecting a suitable indicator of known ionization-constant, using a measured quantity of it, and titrating to a standard color corresponding to the appropriate fraction transformed.

Another, more direct, method of treating the problem of determining the limits between which the indicator-function k may vary when a certain accuracy in the titration is desired is as follows. Representing the limits between which the fractional error permissible in the titration lies by ρ and $-\rho$, substituting $\pm\rho$ for FE in equation (31), and transforming, we get:

$$\frac{K_wK_A}{K_B}\left(\frac{1 + K_B/\gamma C}{1 + K_A/\gamma C}\right) = k^2 \pm \frac{\rho K_A}{\gamma(1 + K_A/\gamma C)}\,k.$$

Adding $\frac{\rho^2 K_A{}^2}{4\gamma^2(1 + K_A/\gamma C)^2}$ to both members to complete the square in the second member, taking the square-root of both members, and transforming, we get the following exact expression:

$$k\,{}^{(\mathrm{Max.})}_{(\mathrm{Min.})} = \frac{\rho K_A}{2\gamma(1 + K_A/\gamma C)} \times \left(\pm 1 + \sqrt{1 + \frac{4\gamma^2}{\rho^2}\,\frac{K_w}{K_AK_B}(1 + K_A/\gamma C)(1 + K_B/\gamma C)}\right). \quad (36)$$

The second term under the square-root sign is considerably smaller than unity in any case in which the titration is practicable. Thus it may be seen from column (1) of Table 1, when $\rho = 0.001$, $C = 0.05$, and K_A or $K_B = 1$, and k_0/k or $k/k_0 > 2.7$, that K_w/K_AK_B must be less than 10^{-8}; under these circumstances, however, the value of the second term in question is less than 0.72. In this case (where $K_w/K_AK_B < 10^{-8}$) it can readily be shown that expression (36) reduces to the following approximate, but sufficiently accurate forms:[1]

---

[1] This follows from the fact that $(1 + x)^{\frac{1}{2}}$ = approx. $(1 + {}^1/_2x)$, when x is small. The whole parenthesis in (36) then has a maximum value of $1 + 1 + \frac{1}{2}x$ = approx. 2, and a minimum value of approx. $-1 + 1 + \frac{1}{2}x$ = approx. $\frac{1}{2}x$, where x represents the second term under the square-root sign. Even in the limiting case where $x = 0.72$ the error in the maximum and minimum values of k when calculated by the approximate expressions (37) and (38) would be only 13 and 16 per cent. respectively.

$$k < \frac{\rho K_A}{\gamma(1 + K_A/\gamma C)}. \tag{37}$$

$$k > \frac{\gamma K_W(1 + K_B/\gamma C)}{\rho K_B}. \tag{38}$$

By means of these expressions the limits between which k must lie in order to give any desired accuracy ρ can evidently be calculated for any given values of K_W, K_A, K_B, and C.[1]

Expressions (37) and (38) show that the lower limit for k is determined by the ionization constant (K_B) of the base, and the upper limit by the ionization-constant (K_A) for the acid.

It is also worthy of note that, since the maximum value of K_B or K_A possessed by any base or acid is unity, since the concentration of the titrated solution can hardly in practice be made greater than 0.5 normal, and since an accuracy at least as great as 1/3 per cent. is almost always essential, the indicator-function k must at 25° under all circumstances have a value lying between the limits of 10^{-3} and 10^{-11}, and the ionization-constant of the indicator must have such a value as will make this possible.

In the important case in which K_A or K_B is even moderately small, say less than 0.1 C, the corresponding expression (37) or (38) remains sufficiently accurate for practical purposes, when written in the still simpler, easily remembered form:

$$k < \rho K_A; \text{ or } k > \frac{K_W}{\rho K_B}. \tag{39}$$

That is, in titrating any not largely ionized acid, the value of the indicator-function must be less than the product of the ionization-constant of the acid by the fractional error permissible in the titration; and in titrating any not largely ionized base, the value of the indicator-function must be greater than the ratio of the ionization-constant of water to the product of the ionization-constant of the base by the fractional error permissible in the titration.

12. *Limits beyond which the Titration is Impracticable.*—Considered from the converse point of view, equation (35) may be utilized to furnish an estimate of the minimum values below which the ionization-constants of the acid and base may not fall if the error in the titration is to be less than any assigned value ρ. For if we represent by β the smallest value

---

[1] As an example, consider first that acetic acid ($K_A = 1.8 \times 10^{-5}$) is to be titrated with potassium hydroxide ($K_B = 1$) at 25° ($K_W = 10^{-14}$) with an accuracy of 0.1 per cent. ($\rho = 0.001$), the resulting salt solution being 0.05 normal ($C = 0.05$ and $\gamma = 0.86$). By substituting these values in (37) and (38) we get:

$$k < 2.1 \times 10^{-8}, \text{ and } k > 2.1 \times 10^{-10}.$$

Consider secondly that ammonium hydroxide ($K_B = 1.8 \times 10^{-5}$) is to be titrated with hydrochloric acid ($K_A = 1$) under the same conditions. We then find:

$$k < 4.8 \times 10^{-5}, \text{ and } k > 4.8 \times 10^{-7}.$$

of $(k_0/k - k/k_0)$ that one can hope to realize in practice, even when reasonable care is taken in choosing a suitable indicator and in securing the proper fraction transformed, equation (35) may be replaced by the following expression:

$$\frac{K_w}{K_A K_B}\gamma^2(1 + K_A/\gamma C)(1 + K_B/\gamma C) < \frac{\rho^2}{\beta^2}. \qquad (40)$$

Since one can hardly count on making k_0/k or k/k_0 less than 3.5,[1] and since in this case $\beta^2 = 10$, we may conclude that the first member of the preceding inequality must always be less than $^1/_{10}\,\rho^2$; that is, less than 10^{-7} for $\rho = {}^1/_{10}$ per cent., less than 10^{-6} for $\rho = {}^1/_3$ per cent., and less than 10^{-5} for $\rho = 1$ per cent. If, furthermore, either the acid or base is nearly completely ionized (K_A or $K_B = 1$) and the concentration C of the titrated solution is not greatly different from 0.1 normal, we may assign the medium value 10 to the product of the last three factors in the first member of (40), and write the inequality in the simple form:

$$\frac{K_w}{K_A K_B} < \frac{1}{100}\rho^2.$$

From this it follows that at 25°, where $K_w = 10^{-14}$, the product $K_A K_B$ must not have a smaller value than 10^{-6}, 10^{-7}, or 10^{-8} if an accuracy of $^1/_{10}$, $^1/_3$, or 1 per cent., respectively, is to be secured. These values therefore represent the practical limits below which the ionization-constant (K_A or K_B) of an acid or base may not fall if it is to be titrated at 25° with the stated accuracy, even with one of the most largely ionized bases or acids, such as sodium hydroxide or hydrochloric acid (for which K_B or K_A = approx. 1).

III. Titration of Two Monobasic Acids or of Two Monacidic Bases in the Presence of Each Other.

13. *Separate Titration of the More Ionized Acid.*—A special case that occurs not infrequently in practice is the titration of an acid HA in the presence of another, much less ionized acid HA′, or of a base BOH in the presence of another, much less ionized base B′OH. It is therefore of interest to determine the conditions under which such a titration can be

---

[1] That this is a reasonable estimate will be seen from the following considerations. It has already been pointed out in discussing equation (34) that the deviation of k_0/k or k/k_0 from unity is likely to arise mainly from the error in the value of K_I assumed in the calculation of the best value of α, and from the error in the experimental realization of the so-calculated value of α. Now there are probably few indicators for which we know the ionization-constant more closely than within one-half or twice its true value; and without taking unusual care in the titration to match the color of the indicator with a standard we can hardly realize any desired value of $(1 - \alpha)/\alpha$ nearer than within one-half or twice that value: and from the combination of these two errors a value of k_0/k or k/k_0 as large as 3.5 is not unlikely to arise. This becomes even more probable when the error likely to be involved in the ionization-constants of very weak bases or acids is also considered.

made without incurring a fractional error greater than any assigned value, especially for the case where a nearly completely ionized base BOH or acid HA is employed as the standard solution.

A general expression for the fractional error analogous to (31) can be readily derived for the case of the two acids in an entirely similar manner, as follows.

It will be noted that the following condition equations corresponding to (22), (23) and (24) hold true in this case:

$$(\Sigma B) = (B^+) + (BOH) + (BA) + (BA'). \qquad (41)$$

$$(\Sigma A) = (A^-) + (HA) + (BA). \qquad (42)$$

$$(B^+) + (H^+) = (A^-) + (A'^-) + (OH^-). \qquad (43)$$

Combining these equations, we get:

$$(\Sigma B) - (\Sigma A) = (BOH) - (HA) + (A'^-) + (BA') + (OH^-) - (H^+). \quad (44)$$

In this case we have to consider also the additional equilibrium equation:

$$(H^+)\,(A'^-) = K_{A'}(HA'). \qquad (45)$$

Since we may without serious error put (HA′) = (ΣA′) or = C' when only an inconsiderable proportion of the acid HA′ is converted into its salt, (45) may be written also in the form:

$$(A'^-) = C'K_{A'}/k. \qquad (46)$$

Dividing both members of (44) by (ΣB), substituting $(A'^-)/\gamma$ for $(A'^-) + (BA')$, eliminating (A'^-) by means of (46), writing C for (ΣB) and (ΣA), expressing the other quantities as before in terms of the appropriate constants, and transforming, we get:

$$\overline{FE} = \frac{(\Sigma B) - (\Sigma A)}{(\Sigma B)} = \frac{\gamma K_w(1 + K_B/\gamma C)}{kK_B} + \frac{C'K_{A'}}{\gamma Ck} - \frac{\gamma k(1 + K_A/\gamma C)}{K_A}. \qquad (47)$$

It will be seen that this equation differs from (31) only in the respect that it contains the additional term $+ C'K_{A'}/\gamma Ck$. (In this term C'/C is equal to the ratio of the quantities of two acids HA′ and HA originally present, and $K_{A'}$ is the ionization-constant of the acid HA′.)

Exact expressions for the best value and the limiting values of the indicator-function can therefore be written down simply by replacing in expressions (33) to (40) the quantity

$$\frac{\gamma K_w(1 + K_B/\gamma C)}{K_B} \text{ by } \frac{C'K_{A'}}{\gamma C} + \frac{\gamma K_w(1 + K_B/\gamma C)}{K_B}.$$

Instead of reproducing these somewhat complex exact expressions here, the simpler approximate expressions may be considered that are applicable: first, to the case where the first term in the last expression is smaller than one-tenth of the second term; and second, to the case where the first term is larger than the second term; so that the smaller of these two terms may be neglected without serious error.

In the first case, where

$$\frac{C'K_{A'}}{C} < \frac{\gamma^2 K_w(1 + K_B/\gamma C)}{10K_B}, \text{ or } < 10^{-14} \text{ at } 25° \text{ when } K_B = 1 \text{ and } C = 0.1,$$

the presence of the acid HA′ evidently has only a relatively small effect on the result of the titration, and no large error will be made by neglecting the term containing $K_{A'}$ and by employing equations (33) to (39), for computing the best value and the limiting values of the indicator-function. This merely signifies that at 25° the presence of an acid whose ionization-constant is less than about 10^{-14} can be disregarded (unless its concentration C' is much larger than that C of the acid to be titrated.)

In the second case, where

$$\frac{C'K_{A'}}{C} > \frac{10\gamma^2 K_w(1 + K_B/\gamma C)}{K_B}, \text{ or } > 10^{-12} \text{ at } 25° \text{ when } K_B = 1 \text{ and } C = 0.1,$$

a large error will not be made by neglecting in (47) the term containing K_w and K_B in comparison with that containing $K_{A'}$. When this is done equation (47) becomes:

$$\text{FE} = \frac{C'K_{A'}}{\gamma Ck} - \frac{\gamma k(1 + K_A/\gamma C)}{K_A}. \qquad (48)$$

Putting FE = 0 and solving for k, we get for the best value of the indicator-function:

$$k_0 = \frac{1}{\gamma}\left(\frac{C'K_{A'}K_A}{C(1 + K_A/\gamma C)}\right)^{\frac{1}{2}}. \qquad (49)$$

The expressions for the limiting values of k which will give a fractional error not greater than ρ are found, for any case in which the titration is practicable, to be as follows:

$$k < \frac{\rho K_A}{\gamma(1 + K_A/\gamma C)} \quad (50); \qquad \text{and } k > \frac{C'K_{A'}}{\rho\gamma C}. \qquad (51)$$

The following expression for FE in terms of k_0/k is also readily obtained from (48) and (49):

$$\text{FE} = \left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{C'K_{A'}}{CK_A}\right)^{\frac{1}{2}}\left(1 + \frac{K_A}{\gamma C}\right)^{\frac{1}{2}}. \qquad (52)$$

From this equation, if we represent by ρ the fractional error permissible in the titration and by β the smallest value of $(k_0/k) - (k/k_0)$ that one can hope to realize, we may obtain by substitution the following expression showing the limiting condition at which the titration ceases to be practicable:

$$\frac{C'K_{A'}}{CK_A}(1 + K_A/\gamma C) < \frac{\rho^2}{\beta^2}. \qquad (53)$$

Assuming $\beta = 3.5$ it follows from this expression for the case that $K_A = 1$

and C = about 0.1 that $C'K_{A'}/CK$ must be less than 10^{-8}, 10^{-7}, and 10^{-6} for accuracies in the titration of $^1/_{10}$, $^1/_3$, and 1 per cent., respectively; and for the case that $K_A < {}^1/_{10}C$ (when the parenthesis becomes substantially equal to unity), that $C'K_{A'}/CK_A$ must be less than 10^{-7}, 10^{-6}, and 10^{-5} for accuracies of $^1/_{10}$, $^1/_3$, and 1 per cent., respectively.

If the two acids were originally present in equivalent quantities ($C = C'$), these same statements are approximately true of the ratio $K_{A'}/K_A$.[1]

14. *Separate Titration of the More Ionized Base.*—The corresponding case involving the titration of a base BOH of ionization-constant K_B and concentration C in the presence of another much less ionized base B'OH of ionization-constant $K_{B'}$ and concentration C' with a nearly completely ionized acid HA can be similarly treated. The resulting expression for the fractional error corresponding to (47) is

$$FE = \frac{\gamma K_W(1 + K_B/\gamma C)}{kK_B} - \frac{\gamma k(1 + K_A/\gamma C)}{K_A} - \frac{kC'K_{B'}}{\gamma CK_W}. \qquad (54)$$

In the case where

$$\frac{C'K_{B'}}{C} < \frac{\gamma^2 K_W(1 + K_A/\gamma C)}{10K_A} \text{ or } < 10^{-14} \text{ at } 25^\circ \text{ when } K_A = 1 \text{ and } C = 0.1,$$

the influence of the base B'OH on the titration can without serious error be disregarded.

In the case where

$$\frac{C'K_{B'}}{C} > \frac{10\gamma^2 K_W(1 + K_A/\gamma C)}{K_A}, \text{ or } < 10^{-12} \text{ at } 25^\circ \text{ when } K_A = 1 \text{ and } C = 0.1,$$

the middle term in the second member of equation (54) is relatively small, and that equation assumes the approximate form:

$$FE = \frac{\gamma K_W(1 + K_B/\gamma C)}{kK_B} - \frac{kC'K_{B'}}{\gamma CK_W}. \qquad (55)$$

The best values and limiting values corresponding to this case are:

$$k_0 = \gamma K_W\left(\frac{C(1 + K_B/\gamma C)}{C'K_{B'}K_B}\right)^{\frac{1}{2}}. \qquad (56)$$

$$k < \frac{\rho\gamma CK_W}{C'K_{B'}} \quad (57); \qquad \text{and } k > \frac{\gamma K_W(1 + K_B/\gamma C)}{\rho K_B} \qquad (58)$$

It can also be readily shown that, as in the case of the two acids, the titration will be practicable with accuracies of $^1/_{10}$, $^1/_3$, and 1 per cent.

---

[1] Thus the ionization-constant for the first hydrogen of carbonic acid, according to Walker and Cormack, is 3 × 10^{-7}. Hence only the most completely ionized acids for which $K_A = 1$, such as HCl and HNO_3, can be titrated at 25° in the presence of an equal number of mols of H_2CO_3, and these only with an accuracy of about $^1/_2$ per cent., even where care is taken to secure a value of k not greater than about 3.5 k_0 and not less than about $^1/_{2.5}$ k_0. The best value k_0 for this case is calculated by equation (49) to be 2.1 × 10^{-4} (for $C = C'$ = about 0.1).

only when $C'K_{B'}/CK_B$ is less than 10^{-8}, 10^{-7}, and 10^{-6} when $K_B = 1$, and less than 10^{-7}, 10^{-6}, and 10^{-5} when $K_B < {}^1/_{10}\gamma C$.

15. *Titration of the Less Ionized Acid or Base.*—It is evident, in the titration of a mixture of two acids HA and HA′ with a largely ionized base, or of two bases BOH and B′OH with a largely ionized acid, that the more ionized acid HA or base BOH will first be converted into its salt, after which the titration of the less ionized acid HA′ or base B′OH will take place substantially as if it had been alone present.[1] The error in its titration, the conditions under which it is practicable, and the best value and limiting values of the indicator-function will therefore be determined by the considerations presented in Part II. Thus in accordance with expressions (39) it is necessary for the titration of HA′ that $k < \rho K_{A'}$, and for the titration of B′OH that $k > \dfrac{K_W}{\rho K_{B'}}$; and in accordance with equation (40) and the discussion following it, it is practically necessary that at 25° at 0.1 normal $K_{A'}$ or $K_{B'}$ be not smaller than 10^{-6}, 10^{-7}, and 10^{-8} for accuracies of $^1/_{10}$, $^1/_3$, and 1 per cent.

It is to be noted that an indicator-function which will give accuracy in the titration of HA′ or B′OH will also be suitable for the titration of the more ionized acid HA or base BOH; and that therefore the sum of the quantities of the two acids or bases can be accurately determined provided the conditions are such that the quantity of the less ionized acid or base can be so determined.

In order that, with the aid of two indicators, the quantity of each of the two acids or each of the two bases may be separately determined with any given accuracy, their ionization-constants must be sufficiently different to satisfy the requirement stated at the end of Sections 13 and 14; and yet, as just stated, the ionization-constant $K_{A'}$ or $K_{B'}$ of the less ionized acid or base must be large enough to satisfy equation (40), namely, at 25° and 0.1 normal it must be as large as 10^{-6}, 10^{-7} and 10^{-8} for accuracies of $^1/_{10}$, $^1/_3$ and 1 per cent. It follows from these two requirements that at 25° when $C = C' = 0.1$ normal, for an accuracy of $^1/_3$ per cent. (the greatest attainable under any conditions), the ionization-constant K_A or K_B of the more ionized acid or base must be as large as unity, and that $K_{A'}$ or $K_{B'}$ of the less ionized acid or base must be in the neighborhood of 10^{-7}; also that for an accuracy of 1 per cent., K_A or K_B may lie between 1 and 10^{-3} and $K_{A'}$ or $K_{B'}$ between 10^{-6} and 10^{-8} provided the ratio between them is as large as 10^5.

IV. Titration of Dibasic Acids with Monacidic Bases.

16. *General Formulation of the Theory.*—Thus far only monobasic acids and monacidic bases have been discussed. The case may now be

---

[1] The neutral salt BA present will not affect the result materially, since it is a salt of the acid HA and not of HA′, or of the base BOH and not of B′OH.

considered in which the acid has two replaceable hydrogens, as indicated by the symbol H_2A. In this case, the condition equations, corresponding to (22), (23), and (24) evidently are:[1]

$$(\Sigma B) = (B^+) + (BOH) + (BHA) + 2(B_2A). \qquad (59)$$

$$(\Sigma A) = (A^=) + (HA^-) + (H_2A) + (BHA) + (B_2A). \qquad (60)$$

$$(B^+) + (H^+) = (HA^-) + 2(A^=) + (OH^-). \qquad (61)$$

17. *Error in the Titration of the First Hydrogen.*—To derive an expression for the titration of the first hydrogen, we may first subtract (60) from (59) and substitute in the result for (B^+) its value given by (61), whereby we get:

$$(\Sigma B)-(\Sigma A) = (BOH) + (A^=) + (B_2A) - (H_2A) + (OH^-) - (H^+). \qquad (62)$$

It is now to be noted that, when (ΣB) is equal or nearly equal to (ΣA), as it is in even a rough titration of the first hydrogen, this equation represents the condition in which the acid H_2A has been nearly completely converted into its acid salt BHA. It is therefore true that $(A^=)$ is a relatively small quantity. We may therefore, when the difference between them is not involved, place $(B^+) = (HA^-)$, thus neglecting in this case the quantities $2(A^=) + (OH^-) - (H^+)$ in equation (61). We may therefore divide all the terms of equation (62) either by (HA^-) or by its substantial equivalent (B^+), whereby we get:

$$\frac{(\Sigma B)-(\Sigma A)}{(B^+)} = \frac{(BOH)}{(B^+)} + \frac{(A^=)+(B_2A)}{(HA^-)} - \frac{(H_2A)}{(HA^-)} + \frac{(OH^-)}{(B^+)} - \frac{(H^+)}{(HA^-)}. \qquad (63)$$

Other expressions for the ratios in the second member may be obtained from the following equations:

$$\frac{(B^+)(OH^-)}{(BOH)} = K_B \quad (64); \qquad \frac{(H^+)(HA^-)}{(H_2A)} = K_{A_1} \quad (65);$$

$$\frac{(H^+)(A^=)}{(HA^-)} = K_{A_2} \quad (66); \qquad (H^+)(OH^-) = K_w \quad (67);$$

$$(H^+) = k \quad (68); \text{ and } \quad (A^=) + (B_2A) = (A^=)/\gamma_2 \quad (69);$$

where k is the indicator-function defined as before by equation (14), and γ_2 is the ionization of the salt B_2A of the unibivalent type.[2]

---

[1] The assumption is here made that the concentration of the intermediate ion BA^- is negligible. There is as yet no evidence that such ions exist in appreciable quantity in the case of salts, at any rate up to moderate concentrations.

[2] Unibivalent salts differ from one another in ionization more than uniunivalent ones. The following average values are, however, sufficiently accurate for the purposes here under discussion:

Normal concentration.............	0.50	0.20	0.10	0.05	0.02	0.01
Ionization γ_2....................	0.50	0 64	0.72	0.76	0.85	0.88

Making obvious substitutions, writing $\gamma_1 C$ for (B^+) and (HA^-), multiplying both members by γ_1, and uniting the first and fourth and the third and fifth terms, equation (63) becomes:

$$\overline{FE} = \frac{(\Sigma B) - (\Sigma A)}{(\Sigma B)} = \frac{\gamma_1 K_w(1 + K_B/\gamma_1 C)}{kK_B} + \frac{\gamma_1 K_{A_2}}{\gamma_2 k} - \frac{\gamma_1 k(1 + K_{A_1}/\gamma_1 C)}{K_{A_1}}. \quad (70)$$

18. *Best Value and Limiting Values of the Indicator-Function for Titration of the First Hydrogen.*—It will be noticed that equation (70) differs from equation (31) only in the respect that it contains the additional term $(+\gamma_1 K_{A_2}/\gamma_2 k)$. By considering this term associated with the positive term preceding it, which also contains k in the denominator, and which therefore can be treated like it in deriving expressions for k, we may write down at once relations corresponding to (33) to (40). More specifically stated, this may be done by substituting in those equations for the quantity

$$\frac{K_w(1 + K_B/\gamma_1 C)}{K_B}, \text{ the quantity } \frac{K_w(1 + K_B/\gamma_1 C)}{K_B} + \frac{K_{A_2}}{\gamma_2}$$

It is therefore not necessary to write out these exact general expressions. We will, however, consider the two following cases: (1) that in which the second term in the last quantity is much smaller, and (2) that in which it is much larger than the first term; so that a serious error will not be made by neglecting the smaller of the two terms. It may be assumed that the error will be negligible when one term is as small as one-tenth of the other.

In the case where

$K_{A_2} < \frac{1}{10}\gamma_2(K_w/K_B)(1+K_B/\gamma_1 C)$, or $< 10^{-14}$ at 25° when $K_B = 1$ and $C = 0.1$, the acid may be treated as a monobasic acid, the ionization of its second hydrogen being disregarded.

In the case where

$K_{A_2} > 10\gamma_2(K_w/K_B)(1+K_B/\gamma_1 C)$ or $> 10^{-12}$ at 25° when $K_B = 1$ and $C = 0.1$, the approximate, but sufficiently accurate expressions for the best value and limiting values of the indicator-function corresponding to (33), (37), and (38) are as follows:

$$k_0 = \left(\frac{K_{A_1}K_{A_2}}{\gamma_2(1 + K_{A_1}/\gamma_1 C)}\right)^{\frac{1}{2}}. \quad (71)$$

$$k < \frac{\rho K_{A_1}}{\gamma_1(1 + K_{A_1}/\gamma_1 C)} \quad (72); \quad \text{and } k > \frac{\gamma_1 K_{A_2}}{\gamma_2 \rho}. \quad (73)$$

In the case, usual with dibasic acids, in which the first hydrogen is only moderately dissociated (thus where $K_{A_1} < {}^1/_{10}\, C$), equation (71) is substantially accurate in the still simpler form:

$$k_0 = \sqrt{K_{A_1}K_{A_2}}. \qquad (74)$$

It is evident therefore that, provided the second hydrogen is appreciably dissociated, it is the product $K_{A_1}K_{A_2}$ which mainly (equation (71)) or wholly (equation (74)) determines the best value of the indicator-function for the titration of the first hydrogen.[1]

In this case (where $K_{A_1} < {}^1/_{10}\,C$) the expressions for the limiting values permissible assume the following approximate, but sufficiently accurate forms:

$$k < \frac{\rho K_{A_1}}{\gamma_1}, \text{ and } k > \frac{\gamma_1 K_{A_2}}{\gamma_2 \rho}. \qquad (75)$$

Thus the smallest value which k may have is determined by the ionization-constant for the second hydrogen, and the largest value by that for the first hydrogen.

In analogy with equation (35), the expression for the fractional error in the titration of the first hydrogen of a dibasic acid may be written in the following form in the case where $K_{A_2} > 10(K_w/K_B)(1 + K_B/\gamma_1 C)$:

$$\overline{\text{FE}} = \gamma_1 \left(\frac{k_0}{k} - \frac{k}{k_0}\right) \left(\frac{K_{A_2}}{\gamma_2 K_{A_1}}\right)^{\frac{1}{2}} (1 + K_{A_1}/\gamma_1 C)^{\frac{1}{2}}. \qquad (76)$$

It is therefore in this case the quantity K_{A_2}/K_{A_1} (instead of $K_w/K_A K_B$) that mainly determines how large the value of k_0/k or k/k_0 may be without causing the fractional error in the titration to exceed any assigned value. Therefore column (3) of Table I in Section 11 will show the maximum values of k_0/k or k/k_0 permissible, if an accuracy of 0.1 per cent. is to be secured in the titration of the first hydrogen of a dibasic acid (for which $K_{A_1} < {}^1/_{10}\,C$ and $K_{A_2} > 10^2 K_w$) with a nearly completely ionized base, if it be understood that the figures in the columns headed $K_w/K_A K_B$ are in this case the values of K_{A_2}/K_{A_1}.

In analogy with expression (40), we may derive from (76) the following expression showing the condition that must be fulfilled in order that the titration may be practicable with any given accuracy ρ:

$$\frac{K_{A_2}}{K_{A_1}} \left(\frac{\gamma_1^2}{\gamma_2}\right) (1 + K_{A_1}/\gamma_1 C) < \frac{\rho^2}{\beta^2} \qquad (77)$$

Assuming as before that β_2 can hardly be made smaller than 10 and that

---

[1] Thus in the case of carbonic acid, for which the ionization-constants for the two hydrogens are $K_{A_1} = 3 \times 10^{-7}$ and $K_{A_2} = 3 \times 10^{-11}$, the best value for the indicator-function is $k_0 = (3 \times 10^{-7} \times 3 \times 10^{-11})^{\frac{1}{2}} = 3 \times 10^{-9}$. In the case of phosphoric acid, for which according to Abbott and Bray (THIS JOURNAL, 31, 760 (1909)) $K_{A_1} = 10^{-2}$ and $K_{A_2} = 2 \times 10^{-7}$, one finds by equation (71) for $C = 0.05$ that

$$k_0 = \left(\frac{K_{A_1}K_{A_2}}{1 + 10^{-2}/(0.86 \times 0.05)}\right)^{\frac{1}{2}} = 0.90(K_{A_1}K_{A_2})^{\frac{1}{2}} = 4.0 \times 10^{-5}.$$

(In the case of tribasic acids, the ionization of the third hydrogen is so much smaller than that of the second hydrogen that it does not affect appreciably the conditions determining the titration of the first hydrogen.)

$K_{A_1} < {}^1/_{10}C$, it follows (since γ_1^2/γ_2 = approx. 1) that the titration can not be made with an accuracy as great as ρ unless $K_{A_2}/K_{A_1} < {}^1/_{10}\rho^2$. Therefore K_{A_2}/K_{A_1} must be less than 10^{-7}, 10^{-6}, and 10^{-5} for accuracies of ${}^1/_{10}$, ${}^1/_3$, and 1 per cent. respectively.[1]

19. *Error in the Titration of the Total Hydrogen.*—An expression applicable to the titration of the total hydrogen may be obtained in a similar way. Namely, by multiplying equation (60) through by 2, subtracting the result from equation (59), and substituting for (B^+) the value of it given by equation (61), we get:

$$(\Sigma B) - 2(\Sigma A) = (BOH) - (HA^-) - (BHA) - 2(H_2A) + (OH^-) - (H^+). \quad (78)$$

Taking into account the fact that in this case (HA^-) is small, so that (B^+) may be placed equal to $2(A^=)$ when the difference between them is not involved, dividing through by (B^+) or its substantial equivalent $2(A^=)$, and putting $(HA^-) + (BHA) = (HA^-)/\gamma_1$ we get:

$$\frac{(\Sigma B) - 2(\Sigma A)}{(B^+)} = \frac{(BOH)}{(B^+)} - \frac{(HA^-)}{2\gamma_1(A^=)} - \frac{(H_2A)}{(A^=)} + \frac{(OH^-)}{(B^+)} - \frac{(H^+)}{2(A^=)}. \quad (79)$$

Substituting for the ratios in the second member their values as given by equations (64) to (68) and for (B^+) or $2(A^=)$ the quantity $\gamma_2 C$ (where C therefore represents the *equivalent* concentration of the salt), and multiplying through by γ_2, the ionization of the unibivalent salt, we get:

$$\frac{(\Sigma B) - 2(\Sigma A)}{(\Sigma B) \text{ or } 2(\Sigma A)} = \gamma_2\left(\frac{K_w}{kK_B} - \frac{k}{2\gamma_1 K_{A_2}} - \frac{k^2}{K_{A_1}K_{A_2}} + \frac{K_w}{k\gamma_2 C} - \frac{k}{\gamma_2 C}\right). \quad (80)$$

This equation evidently expresses the fractional error in the titration of the total hydrogen in the ordinary case in which no salt of the acid or base is originally present in the solutions.

Since equation (80) is a cubic with respect to k, a rigorous discussion of the best value and of the limiting values of the indicator-function would be attended with mathematical difficulties. It is therefore of importance to note that the third term in the parenthesis is in practice entirely negligible in comparison with the second term, whenever even a very rough titration is possible. This is true since the ratio of the third to the second term is $2\gamma_1 k/K_{A_1}$, since it may be shown (by substituting $2\gamma K_{A_2}$ for K_A in (37)) that $k/2K_{A_2}$ must be less than the fractional error, and since for all dibasic acids K_{A_1} is much larger than K_{A_2}. (Considered from the standpoint of the chemical composition as expressed by equation (78), this signifies that $2(H_2A)$ is negligible in comparison with (HA^-) in a solution in which the acid has been almost wholly converted into the salt B_2A or its ions.) Neglecting the third term in the parenthesis and writing $\overline{FE}$ for the first member, equation (80) becomes:

---

[1] Therefore in the case of carbonic acid for which $K_{A_2} = 10^{-4}\,K_{A_1}$ the titration of the first hydrogen is not possible with even a moderate degree of accuracy. But in the case of phosphoric acid, for which $K_{A_2} = 2 \times 10^{-5}\,K_{A_1}$ the titration of the first hydrogen should be possible with an accuracy of not far from 1 per cent by taking care to secure a value of the indicator-function as nearly as possible equal to the best value. In the case of nearly all the organic dibasic acids, the ionization-constants for the first and second hydrogens do not differ from each other sufficiently to make a titration of the former at all possible.

$$\overline{FE} = \frac{\gamma_2 K_W}{kK_B}(1 + K_B/\gamma_2 C) - \frac{\gamma_2 k}{2\gamma_1 K_{A_2}}(1 + 2\gamma_1 K_{A_2}/\gamma_2 C). \quad (81)$$

This will be seen to be identical with equation (31) expressing the error in titrating a monobasic acid, except that it contains $2\gamma_1 K_{A_2}$ in place of K_A, and γ_2 in place of γ. It will also be noted that in the titration of a dibasic acid it is the constants for the base and for the second hydrogen which determine the error, that for the first hydrogen having dropped out.

20. *Best Value and Limiting Values of the Indicator-Function for Titration of the Total Hydrogen.*—In view of the close correspondence of equations (81) and (31) just referred to, all the conclusions drawn from the latter in regard to the best value and the limiting values of the indicator-function for the titration of monobasic acids can be made to apply directly to the titration of the total hydrogen of dibasic acids by substituting $2\gamma_1 K_{A_2}$ for K_A and γ_2 for γ, in expressions (33) to (40), in Table I, and in the discussions of those expressions and of that table. It is therefore unnecessary to consider in detail the conditions relating to the titration of the total hydrogen.

V. Titration of Diacidic Bases with Monobasic Acids.

21. *Error in the Titration of the First Hydroxyl.*—By a method entirely analogous to that just described for dibasic acids expressions may be obtained for the error in the titration of both the first and total hydroxyl of a diacidic base $B(OH)_2$ with a monobasic acid HA, the ionization-constants for the first and second hydroxyls being represented by K_{B_1} and K_{B_2} and defined by the equilibrium equations:

$$\frac{(BOH^+)(OH^-)}{B(OH)_2} = K_{B_1} \quad (82); \qquad \frac{(B^{++})(OH^-)}{(BOH^+)} = K_{B_2}. \quad (83)$$

The so-obtained expression for the first hydroxyl is:

$$FE = \frac{(\Sigma B) - (\Sigma A)}{(\Sigma B) \text{ or } (\Sigma A)} = \frac{\gamma_1 K_W(1 + K_{B_1}/\gamma_1 C)}{kK_{B_1}} - \frac{\gamma_1 k(1 + K_A/\gamma_1 C)}{K_A} - \frac{\gamma_1 k K_{B_2}}{\gamma_2 K_W} \quad (84)$$

22. *Best Value and Limiting Values of the Indicator-Function for Titration of the First Hydroxyl.*—It will be seen that equation (84) corresponds

closely with (70), and differs from (31) only in the respect that it contains the additional term ($-\gamma_1 k K_{B_2}/K_w\gamma_2$). By a treatment entirely analogous to that described in Section 18 expressions may be obtained for the best value and the limiting values of the indicator-function. The following are the forms applicable to the case where

$K_{B_2} \times 10(K_w/K_A)(1+K_A/\gamma_1 C)$ or $> 10^{-12}$ at 25° when $K_A = 1$ and $C = 0.1$:

$$k_0 = \left(\frac{\gamma_2 K_w^2}{K_{B_1}K_{B_2}}\right)^{\frac{1}{2}}(1 + K_{B_1}/\gamma_1 C)^{\frac{1}{2}} = \text{appr.} \frac{K_w}{\sqrt{K_{B_1}K_{B_2}}} \text{ when } K_{B_1} < \frac{1}{10}C. \quad (85)$$

$$k < \frac{\rho\gamma_2 K_w}{\gamma_1 K_{B_2}} \quad (86), \qquad \text{and } k > \frac{\gamma_1 K_w(1 + K_{B_1}/\gamma_1 C)}{\rho K_{B_1}} \quad (87)$$

$$\text{or } k > \frac{\gamma_1 K_w}{\rho K_{B_1}} \text{ when } K_{B_1} < \frac{1}{10}C. \quad (87a)$$

$$\overline{FE} = {}_1\left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{K_{B_2}}{\gamma_2 K_{B_1}}\right)^{\frac{1}{2}}(1 + K_{B_1}/\gamma_1 C)^{\frac{1}{2}}. \quad (88)$$

$$\frac{K_{B_2}\gamma_1^2}{K_{B_1}\gamma_2}(1 + K_{B_1}/\gamma_1 C) < \frac{\rho^2}{\beta^2}. \quad (89)$$

23. *Titration of the Total Hydroxyl.*—For the error in this titration the following expression analogous to equations (31) and (81) may be obtained by a similar method of procedure:

$$\overline{FE} = \frac{\gamma_2 K_w}{2k\gamma_1 K_{B_2}}(1 + 2\gamma_1 K_{B_2}/\gamma_2 C) \quad \frac{\gamma_2 k}{K_A}(1 + K_A/\gamma_2 C). \quad (90)$$

This will be seen to differ from equation (31) only in the respects that it contains $2\gamma_1 K_{B_2}$ in place of K_B, and γ_2 in place of γ. The conclusions drawn from that equation therefore all apply, after making these substitutions, to the titration of the total hydroxyl of a diacidic base.

VI. Summary.

24. *Summary.*—It seems desirable to sum up the conclusions reached in this article which are of most direct application to the problems of volumetric analysis.

The equilibrium relations of the two differently colored structural forms in which all indicators probably exist, and the equilibrium conditions under which such a pair of tautomeric substances can show sharply differentiated colors in acid and alkaline solution were first discussed (see Section 2). It was shown that, provided these conditions are fulfilled, the indicator can be treated in titrations as if it were a single acid or base having an ionization-constant which, though really a function of three equilibrium-constants, can be directly determined either from the color-changes exhibited by it in solutions of various hydrogen-ion concentration, or by any of the other methods commonly employed—for example, by measurement of the conductivity of the indicator acid or base or by a study of the hydrolysis of its salt.

The well-known principle of the theory of indicators was then formulated (in Section 3), according to which the proportion of the indicator acid converted into its salt, or of the indicator base liberated from its salt, is determined solely by its ionization-constant (K_{IA} or K_{IB}) and by the hydrogen-ion concentration (H^+) in the solution; and a series of lecture experiments illustrating this were described in Section 4. Defining the end-point of the titration as the condition where a definite proportion (α) of the indicator, as shown by the color, is so transformed, the equilibrium prevailing at the end-point is then expressed by the equations:

$(H^+) = K_{IA}(1 - \alpha)/\alpha\gamma = k$, for an acid indicator; or

$(H^+) = (K_w/K_{IB})(\gamma(1 - \alpha)/\alpha) = k$, for a basic indicator;

where $K_w = (H^+)(OH^-)$, and γ represents the ionization of the indicator salt, which may be assumed to be equal to that of other salts of the same type.

The symmetry in the equilibrium relations of acid and basic indicators and the impossibility of distinguishing them by their behavior in titrations was pointed out; and the term apparent ionization-constant (K_I) was introduced, this being defined for acid and basic indicators by the equations $K_I = K_{IA}/\gamma$ and $K_I = \gamma K_w/K_{IB}$, respectively, where γ represents the ionization of the indicator salt in any solution in which its color serves as a measure of its concentration We then have for either an acid or basic indicator: $(H^+) = K_I(1 - \alpha)/\alpha = k$.

Throughout the article the letter k is written in place of the lengthy expression preceding it in this equation; and it is designated the indicator-function. This fundamental quantity was fully discussed in Section 5, the fact being emphasized that it depends on two factors, the ionization-constant of the indicator and the fraction of it transformed at the end-point. The limits within which the fraction transformed can be varied in practice were considered, it being pointed out that the experimental determination of these limits for each indicator would supplement in an important way that of its ionization-constant In the absence of such experimental data, it was suggested as a reasonable estimate that in the case of sufficiently soluble one-color indicators, like *p*-nitrophenol, the fraction transformed might be varied from 0.1 to 25 per cent., corresponding to a variation of k from 1000 K_I to $3K_I$. When, however, the indicator has a limited solubility S, the largest value of k that can be secured is equal to $K_I(S - I)/I$, where I represents that concentration of the transformed part of the indicator which gives the depth of color suitable for the end-point. Attention was called to the facts that in the case of two-color indicators, like methyl orange, the range was much smaller, since the fraction transformed must have a considerable value in order that its color may not be entirely obscured by the color of the untransformed part of the indicator; and that, on the other hand, such indicators could sometimes be employed at both ends of their transformation, being in one case say 10 per cent. transformed in the direction from acid to alkaline and in the other case 10 per cent. transformed in the other direction, thus giving two values of k equal to about $10K_I$ and $^1/_{10}K_I$, respectively.

It was shown in Section 6 that, if the indicator itself is not to require for its neutralization an appreciable proportion of the base or acid used in the titration, its concentration (ΣIn) in the titrated solution must be less than $\rho C/\alpha$ for an acid indicator, or less than $\rho C/(1 - \alpha)$ for a basic indicator, where C represents the concentration of the salt, ρ the fractional error permissible in the titration, and α the fraction of the indicator transformed in the direction from acid to alkaline.

Through formulation of the equilibrium and condition equations involved and the combination of these, the following practically exact expression was derived in Sections 7 and 8 for the fractional error $\overline{\mathrm{FE}}$[1] incurred in the titration of any monobasic acid HA of ionization-constant K_A and of any monacidic base BOH of ionization-constant K_B when the indicator-function has any value k, the salt in the titrated solution having an equivalent concentration C and an ionization γ_1:

$$\overline{\mathrm{FE}} = \frac{\gamma K_w}{k K_B}(1 + K_B/\gamma_1 C) - \frac{\gamma k}{K_A}(1 + K_A/\gamma_1 C). \qquad (31)$$

It was shown in Section 9 that, when a neutral salt BA of the acid and base is originally present in the solution to be titrated, the fractional error in the titration is equal to that calculated by equation (31) multiplied by the ratio which the sum of the quantity of that salt and of the quantity of acid or base used in the titration bears to the latter quantity. This also holds true when a neutral salt (BA′ or B′A) is present which is a salt of a different acid or base (HA′ or B′OH) provided the latter is of the largely ionized type.

In later sections were derived expressions for the fractional error in the titration of combinations of other types of acids and bases, as follows:

For the total hydrogen of a dibasic acid H_2A with a monacidic base BOH, replace in (31) K_A by $2\gamma_1 K_{A_2}$ and γ_1 by γ_2. (81)

For the total hydroxyl of a diacidic base $B(OH)_2$ with a monobasic acid HA, replace in (31) K_B by $2\gamma_1 K_{B_2}$ and γ_1 by γ_2. (90)

For the first hydrogen of a dibasic acid H_2A with a monacidic base BOH:

$$\overline{\mathrm{FE}} = \frac{\gamma_1 K_w}{k K_B}(1 + K_B/\gamma_1 C) - \frac{\gamma_1 k}{K_{A_1}}(1 + K_{A_1}/\gamma_1 C) + \frac{\gamma_1 K_{A_2}}{\gamma_2 k}. \qquad (70)$$

---

[1] Meaning thereby the difference between the quantity of acid or base originally present and the quantity of standard base or acid added when the end-point has been reached, divided by either of these quantities. The percentage error is, of course, equal to 100 $\overline{\mathrm{FE}}$.

For the first hydroxyl of a diacidic base $B(OH)_2$ with a monobasic acid HA:

$$\overline{\overline{\mathrm{FE}}} = \frac{\gamma_1 K_w}{kK_{B_1}}(1 + K_{B_1}/\gamma_1 C) - \frac{\gamma_1 k}{K_A}(1 + K_A/\gamma_1 C) - \frac{\gamma_1 k K_{B_2}}{\gamma_2 K_w}. \quad (84)$$

In these expressions K_{A_1} and K_{A_2} represent the ionization-constants for the first and second hydrogens of the acid as defined by the equations $(H^+)(HA^-)/(H_2A) = K_{A_1}$ and $(H^+)(A^-)/(HA^-) = K_{A_2}$, K_{B_1} and K_{B_2}; represent the ionization-constants for the first and second hydroxyls of the base correspondingly defined; C represents the equivalent concentration of the salt in the titrated solution; and γ_1 and γ_2 represent the degrees of ionization in the titrated solution of the salts of the uni-univalent and unibivalent types. Average values of these degrees of ionization at various concentrations will be found in tables given in Sections 8 and 17.

For the titration of a more ionized acid HA in the presence of a less ionized acid HA′ with a monacidic base BOH:

$$\overline{\overline{\mathrm{FE}}} = \frac{\gamma_1 K_w}{kK_B}(1 + K_B/\gamma_1 C) \quad \frac{\gamma_1 k}{K_A}(1 + K_A/\gamma_1 C) + \frac{C' K_{A'}}{\gamma_1 C k}. \quad (47)$$

For the titration of a more ionized base BOH in the presence of a less ionized base B′OH with a monobasic acid HA:

$$\overline{\overline{\mathrm{FE}}} = \frac{\gamma_1 K_w}{kK_B}(1 + K_B/\gamma_1 C) - \frac{\gamma_1 k}{K_A}(1 + K_A/\gamma_1 C) - \frac{k C' K_{B'}}{\gamma_1 C K_w}. \quad (54)$$

The C'/C occurring in the last terms of these equations is equal to the ratio of the quantities of the two acids HA′ and HA, or of the two bases B′OH and BOH, originally present in the solution to be titrated; and $K_{A'}$ and K_A, or K_B and $K_{B'}$, are the ionization-constants of these two acids or bases.

By these expressions the fractional error can be readily calculated in any case where the values of the ionization-constants involved and of the indicator-function are known. The error can evidently be reduced by securing an appropriate value of the indicator-function, which may be done by choosing a suitable indicator and taking care that the proper fraction of it is transformed at the end-point. Other sections of the article are therefore devoted to the derivation of expressions for the best value of the indicator-function and for the limiting values permissible in the different cases, and to a consideration of the conditions, under which the titration ceases to be practicable with any indicator.

By placing in each of the seven equations just considered the first member $\overline{\overline{\mathrm{FE}}}$ equal to zero, and solving the equation for k, expressions were obtained for the value which the indicator-function k must have in order that the titration may be perfect. The expressions for the "best values" (k_0) of k so obtained are for the seven cases as follows:

For the titration of a monobasic acid and a monacidic base:

$$k_o = \left(\frac{K_w(1+K_B/\gamma_1 C)}{K_B}\right)^{\frac{1}{2}} \left(\frac{K_A}{1+K_A/\gamma_1 C}\right)^{\frac{1}{2}}. \qquad (33)$$

For the titration of the total hydrogen of a dibasic acid with a monobasic acid, replace in equation (33) K_A by $2\gamma_1 K_{A_2}$ and γ_1 by γ_2.

For the titration of the total hydroxyl of a diacidic base with a monobasic acid, replace in equation (33) K_B by $2\gamma_1 K_{B_2}$ and γ_1 by γ_2.

For the titration of the first hydrogen of a dibasic acid with a monacidic base, when $K_{A_2} > 10(K_w/K_B)\ (1 + K_B/\gamma_1 C)$:

$$k_o = \left(\frac{K_{A_1}K_{A_2}}{\gamma_2(1+K_{A_1}/\gamma_1 C)}\right)^{\frac{1}{2}}. \qquad (71)$$

For the titration of the first hydroxyl of a diacidic base with a monobasic acid, when $K_{B_2} > 10(K_w/K_A)\ (1 + K_A/\gamma_1 C)$:

$$k_o = \left(\frac{\gamma_2 K_w^2}{K_{B_1}K_{B_2}}\right)^{\frac{1}{2}} (1+K_{B_1}/\gamma_1 C)^{\frac{1}{2}}. \qquad (85)$$

For the titration of a more ionized acid HA in the presence of a less ionized one HA′, when $(K_{A'}C'/C) > 10(K_w/K_B)\ (1 + {}_BK/\gamma_1 C)$:

$$k_o = \frac{1}{\gamma_1}\left(\frac{C'K_{A'}K_A}{C(1+K_A/\gamma_1 C)}\right)^{\frac{1}{2}}. \qquad (49)$$

For the titration of a more ionized base BOH in the presence of less ionized one B′OH, when $(K_{B'}C'/C) > 10(K_w/K_A)\ (1 + K_A/\gamma_1 C)$:

$$k_o = \gamma_1 K_w \left(\frac{C(1+K_B/\gamma_1 C)}{C'K_{B'}K_B}\right)^{\frac{1}{2}}. \qquad (56)$$

The applicability of the last four equations is not greatly limited by the restriction that the ionization-constant for the hydrogen that is *not* to be titrated must be greater than $10(K_w/K_{A \text{ or } B})\ (1 + K_{A \text{ or } B}/\gamma C)$; for this quantity has at 25° (where $K_w = 10^{-14}$) a value of only about 10^{-12} when the titration is made, as it usually is, with an almost completely ionized univalent base or acid (for which K_B or $K_A = 1$), such as sodium hydroxide or hydrochloric acid. (This restriction and these statements in regard to it apply also to the corresponding equations presented below.) If K_{A_2} or K_{B_2} is smaller than $^1/_{100}$ of this quantity (thus smaller than 10^{-14} at 25°) the dibasic acid or diacidic base may be treated as a monobasic or monacidic one; and if $(K_{A'}C'/C)$ or $(K_{B'}C'/C)$ is smaller than $^1/_{100}$ of this quantity, the presence of the less ionized acid or base can be disregarded. In the intermediate case more complex formulas than those given above must be used, in regard to which reference may be made to Sections 18, 22, 13, and 14.

By placing in each of the seven equations for the fractional error the first member $\overline{FE}$ equal to $\pm\rho$ and solving for k, expressions can be directly obtained for the maximum and minimum values which the indicator-function k may have without giving rise to a fractional error numerically greater than any assigned value ρ. The expressions so obtained are:

For the titration of a monobasic acid with a monacidic base, or the reverse:

$$k < \frac{pK_A}{\gamma_1(1+K_A/\gamma_1 C)} \quad (37), \text{ and } k > \frac{\gamma_1 K_w(1+K_B/\gamma_1 C)}{pK_B}. \quad (38)$$

For the titration of the total hydrogen of a dibasic acid, replace in (37) K_A by $2\gamma_1 K_{A_2}$ and γ_1 by γ_2; and for the titration of the total hydroxyl of a diacidic base, replace in (38) K_B by $2\gamma_1 K_{B_2}$ and γ_1 by γ_2.

For the titration of the first hydrogen of a dibasic acid with a nearly completely ionized base:

$$k < \frac{pK_{A_1}}{\gamma_1(1 + K_{A_1}/\gamma_1 C)} \quad (72); \quad \text{and } k > \frac{\gamma_1 K_{A_2}}{\gamma_2 p} \quad (73).$$

For the titration of the first hydroxyl of a diacidic base with a nearly completely ionized acid:

$$k < \frac{\gamma_2 p K_w}{\gamma_1 K_{B_2}} \quad (86); \quad \text{and } k > \frac{\gamma_1 K_w(1 + K_{B_1}/\gamma_1 C)}{pK_{B_1}} \quad (87).$$

For the titration of an acid HA in the presence of another acid HA′, with a nearly completely ionized base:

$$k < \frac{pK_A}{\gamma_1(1 + K_A/\gamma_1 C)} \quad (50); \quad \text{and } k > \frac{C'K_{A'}}{p\gamma_1 C} \quad (51).$$

For the titration of a base BOH in the presence of another base B′OH, with a nearly completely ionized acid:

$$k < \frac{p\gamma_1 C K_w}{C'K_{B'}} \quad (57); \quad \text{and } k > \frac{\gamma_1 K_w(1 + K_B/\gamma_1 C)}{pK_B} \quad (58).$$

By these expressions the practical limits between which the indicator-function must lie can be readily calculated for any given combination of acid and base. It will be observed that in the first three cases, where the total acid or base present is to be titrated, the upper limit for k is determined by the ionization-constant of the acid and the lower limit by that of the base; that, in the case of the titration of the first hydrogen of a dibasic acid or of one monobasic acid in the presence of another, the upper limit is determined by the ionization-constant for the hydrogen that is to be titrated, and the lower limit by that for the hydrogen that is not to be titrated; and that the reverse is true in the case of the titration of the first hydroxyl of a diacidic base, or of one monacidic base in the presence of another.

It has been shown that, although theoretically there is a value of the indicator-function which would make a perfect titration possible for any combination of acid and base, yet in practice, since that best value k_0 can be only approximately realized, it ceases to be possible to make the titration with reasonable accuracy when the ionization-constants of the base and acid assume too small values. The following expressions were derived in order to show how great the ratio of the actual value k to the best value k_0 may become without causing the fractional error in the titration to exceed any assigned value:

For the titration of a monobasic acid and a monacidic base;

$$\text{FE} = \gamma_1\left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{K_W}{K_A K_B}\right)^{\frac{1}{2}}(1 + K_B/\gamma_1 C)^{\frac{1}{2}}(1 + K_A/\gamma_1 C)^{\frac{1}{2}}. \qquad (35)$$

For the titration of the total hydrogen of a dibasic acid or the total hydroxyl of a diacidic base, replace in this equation γ_1 by γ_2 and K_A by $2\gamma_1 K_{A_2}$, or γ_1 by γ_2 and K_B by $2\gamma_1 K_{B_2}$, respectively.

For the titration of the first hydrogen of a dibasic acid:

$$\text{FE} = \gamma_1\left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{K_{A_2}}{\gamma_2 K_{A_1}}\right)^{\frac{1}{2}}(1 + K_{A_1}/\gamma_1 C)^{\frac{1}{2}}. \qquad (76)$$

For the titration of the first hydroxyl of a diacidic base, replace in this equation K_{A_2} by K_{B_2} and K_{A_1} by K_{B_1}. (88)

For the titration of one monobasic acid HA in presence of another, less ionized one HA′,

$$\text{FE} = \left(\frac{k_0}{k} - \frac{k}{k_0}\right)\left(\frac{C'K_{A'}}{CK_A}\right)^{\frac{1}{2}}(1 + K_A/\gamma_1 C)^{\frac{1}{2}}. \qquad (52)$$

For the titration of one monacidic base BOH in presence of another less ionized one B′OH, one should replace $K_{A'}$ by $K_{B'}$ and K_A by K_B in this equation.

Since the factors of the form $(1 + K/\gamma_1 C)^{\frac{1}{2}}$ never have a value very different from unity, how small k_0/k or k/k_0 must be to prevent the error FE from exceeding any assigned value depends mainly on how small the value is of $\frac{K_W}{K_A K_B}$, $\frac{K_W}{2K_{A_2}K_B}$, $\frac{K_W}{2K_A K_{B_2}}$, $\frac{K_{A_2}}{K_{A_1}}$, $\frac{K_{B_2}}{K_{B_1}}$, $\frac{C'K_{A'}}{CK_A}$, or $\frac{C'K_{B'}}{CK_B}$.

The numerical values of k_0/k or k/k_0 corresponding to a fractional error of 0.1 per cent., to a series of values of $K_W/K_A K_B$ or of any other of these seven quantities, and to different values of $(1 + K/\gamma_1 C)$ have been calculated and tabulated on page 836. This table shows that as any of these seven quantities increases, greater care must be taken to bring the actual value k of the indicator-function closer to the best value k_0, and when any of them becomes as large as 10^{-8}, the ratio k_0/k or k/k_0 must be given a value so small as to approach the practically attainable limit; namely, a value less than 7.4 when K_A or $K_B = 1$ and $C = 0.5$, and one less than 2.7 when K_A or $K_B = 1$ and $C = 0.05$. The table, as illustrated by this example, also shows that the smaller the concentration C of the titrated solution, the smaller is the limiting value of k_0/k or k/k_0 at which the titration is still possible with a given accuracy, and therefore that it is advantageous to titrate in a solution as concentrated as possible whenever the titration is sensitive to error and a strong base or acid is involved in it.

It was also pointed out, since the actual value of the indicator-function must be made to approach the best value more closely as K_w/K_AK_B, $K_w/2K_{A_2}K_B$ or $K_w/2K_AK_{B_2}$ increases, and since K_w increases very rapidly with rising temperature (thus from 10^{-15} at 0° to 10^{-14} at 25° and 10^{-13} at 65°), that it is advantageous to make the titration at as low a temperature as possible, provided the total acid or base present is to be titrated.

The following expressions, showing the maximum values which any of the seven quantities above referred to may have without causing the titration to become impracticable, were obtained from the equations for FE by denoting the minimum value of $(k_0/k - k/k_0)$ which one can hope to realize in practice by β and representing the fractional error permissible in the titration by ρ, and transforming:

For the titration of a monobasic acid and monacidic base:

$$\frac{K_W}{K_AK_B}\cdot\gamma_1^2(1+K_A/\gamma_1C)(1+K_B/\gamma_1C)<\frac{\rho^2}{\beta^2}. \qquad (40)$$

For the titration of the first hydrogen of a dibasic acid:

$$\frac{K_{A_2}}{K_{A_1}}\left(\frac{\gamma_1^2}{\gamma_2}\right)(1+K_{A_1}/\gamma_1C)<\frac{\rho^2}{\beta^2}. \qquad (77)$$

For the titration of one monobasic acid HA in the presence of another less ionized one HA′:

$$\frac{C'K_{A'}}{CK_A}(1+K_A/\gamma_1C)<\frac{\rho^2}{\beta^2}. \qquad (53)$$

For the titration of the other combinations the same substitutions are to be made in these expressions as in the previous cases.

It was shown in Section 12 that the smallest value of k_0/k or k/k_0 that one can ordinarily hope to realize may be fairly estimated to be in the neighborhood of 3.5. Since under this assumption β^2 is equal to 10, we may conclude that the first members of the preceding inequalities must not have a larger value than 10^{-7}, 10^{-6}, and 10^{-5} if the error (ρ) in the titration is not to exceed $^1/_{10}$, $^1/_3$, and 1 per cent., respectively.

By the first of these inequalities one can also calculate the minimum value which the product K_AK_B may have under various conditions. It is evident that this minimum value will be smaller, the greater the concentration C of the titrated solution and the lower the temperature (owing to the variation of K_w with the latter). It may also be pointed out that under ordinary conditions (say at 25° with the concentration 0.1 normal) the minimum value which K_A or K_B may have is about 10^{-8}, 10^{-7}, or 10^{-6} if the acid or base is to be titrated with an accuracy of $^1/_{10}$, $^1/_3$, or 1 per cent. with one of the nearly completely ionized bases or acids. The same statements apply to the product $2K_{A_2}K_B$ in the case of a dibasic acid, and to the product $2K_AK_{B_2}$ in the case of a diacidic base; also to the values of $2K_{A_2}$ and $2K_{B_2}$.

The more important of the foregoing considerations relating to the best value and the limiting values of the indicator-function may be expressed in the form of simple practical rules which, though only approximately correct, have sufficient accuracy for almost all purposes. These rules may be derived from the equations for k_0 and from the inequalities containing k and ρ by putting γ equal to unity, by putting also the expressions of the form $1 + K/\gamma C$ equal to unity when they refer to acids or bases that are not largely ionized, and by assigning to expressions of the form $\gamma(1 + K/\gamma C)/K$ the medium value[1] 10 and to K_A or K_B the value unity when they refer to the most completely ionized acids or bases. The rules are as follows:

In order that a not largely ionized acid or base may be titrated with one of the most largely ionized bases or acids with a fractional error not greater than ρ, it is essential that the indicator-function k have a value which is greater than the "minimum value" and less than the "maximum value" given in the following table; and in order to assure the fulfilment of this requirement, it is advisable in any titration sensitive to error to aim to secure a value of the indicator-function as nearly as possible equal to the "best value," whose square is given in the table.[2]

TABLE 2.—APPROXIMATE EXPRESSIONS FOR THE MAXIMUM, MINIMUM, AND BEST VALUES OF THE INDICATOR-FUNCTION.

Titration, with a largely ionized base or acid, of	Square of best value.	Maximum value.	Minimum value.	Function for limit of titratability
A monobasic acid	$10K_WK_A$	ρK_A	$10K_W/\rho$	$10K_W/K_A$
A monacidic base.........	$^1/_{10}K_W/K_B$	$^1/_{10}\rho$	$K_W/(\rho K_B)$	$10K_W/K_B$
The total hydrogen of a dibasic acid.............	$10K_W2K_{A_2}$	$\rho 2K_{A_2}$	$10K_W/\rho$	$10K_W/2K_{A_2}$
The total hydroxyl of a diacidic base.............	$^1/_{10}K_W/2K_{B_2}$	$^1/_{10}\rho$	$K_W/(\rho 2K_{B_2})$	$10K_W/2K_{B_2}$
The first hydrogen of a polybasic acid..........	$K_{A_1}K_{A_2}$	ρK_{A_1}	K_{A_2}/ρ	K_{A_2}/K_{A_1}
The first hydroxyl of a polyacidic base	$\frac{K_W^2}{K_{B_1}K_{B_2}}$	$\frac{\rho K_W}{K_{B_2}}$	$\frac{K_W}{\rho K_{B_1}}$	K_{B_2}/K_{B_1}
One monobasic acid (HA) in the presence of another (HA')............	$\frac{K_AK_{A'}C'}{C}$	ρK_A	$\frac{K_{A'}C'}{\rho C}$	$\frac{K_{A'}C'}{K_AC}$
One monacidic base (BOH) in the presence of another (B'OH)...........	$\frac{K_W^2C}{K_BK_{B'}C'}$	$\rho\frac{CK_W}{C'K_{B'}}$	$\frac{K_W}{\rho K_B}$	$\frac{K_{B'}C'}{K_BC}$

---

[1] When $K = 1$ as it is approximately for such acids as HCl and HNO_3 and such bases as NaOH and KOH at 0.1 normal, the value of $\gamma(1 + K/\gamma C)/K$ varies from about 3 when the titrated solution is 0.5 normal, to about 21 when it is 0.05 normal.

[2] For the significance of the various K's and C's in this table see the third and fourth pages of this Summary. For an example illustrating the use of the table, see the foot-note at the end of the article.

The table also contains in the last column that function of the ionization-constants whose value determines the limit beyond which the titration becomes impracticable. This limit depends also on how small a value of $(k_0/k - k/k_0)$ it is possible to realize. If we represent by β the minimum value of the latter quantity attainable, the following rule in regard to the limit may be stated:

In order that the titration of a not largely ionized acid or base with one of the most completely ionized bases or acids may be made with a fractional error not greater than ρ, it is essential that the quantity given in the last column of the table have a value less than that of the ratio ρ^2/β^2. If we adopt the estimate that the value of k_0/k or k/k_0 may be made as small as 3.5, but not smaller without taking unusual precautions, then $\beta^2 = 10$ approximately; and we may conclude that the titration ceases to be practicable with an accuracy ρ when any of the functions of the ionization-constants given in the preceding list become greater than $^1/_{10}\rho^2$; thus greater than 10^{-7} for an accuracy of $^1/_{10}$ per cent., greater than 10^{-6} for an accuracy of $^1/_3$ per cent., and greater than 10^{-5} for an accuracy of 1 per cent.

VII. Appendix.

25. *Values of the Ionization-Constants of Indicators.*—The application of the principles developed in this article to the various practicable titrations involves the use of a series of indicators with ionization-constants varying in value by gradations from about 10^{-3} to 10^{-11}. Unfortunately, our knowledge of the ionization-constants of the numerous available indicators is at present for the most part inexact, and needs to be supplemented by further careful investigations. Extensive preliminary studies of indicators in this direction were first made by Friedenthal,[1] Salessky,[2] Fels,[3] and Salm,[4] who have published tables showing roughly the hydrogen-ion concentration at which a large number of indicators undergo change in color, in connection with which it may be recalled that the ionization-constant of an indicator is equal to the hydrogen-ion concentration at which it is one-half transformed into its salt. A more careful investigation by the colorimetric method has been made by Salm[5] with the object of obtaining better values of the constants for several of the more important indicators. A quantitative study of phenolphthalein has also been

---

[1] *Z. Elektrochem.*, 10, 113 (1904).

[2] *Ibid.*, 10, 204 (1904).

[3] *Ibid.*, 10, 208 (1904).

[4] *Ibid.*, 10, 344 (1904).

[5] *Z. physik. Chem.*, 57, 492–7 (1907).

made colorimetrically by McCoy,[1] Hildebrand,[2] and Wegscheider;[3] and the ionization-constant for *p*-nitrophenol has been determined by the ordinary conductivity method by Bader,[4] Hantzsch,[5] Holleman,[6] and Lundén.[7]

The following table contains the values of the apparent indicator-constant K_I (as defined at the end of Section 3) derived from these quantitative investigations, the data being those of Salm, except in the case of phenolphthalein where the geometrical mean of the values obtained by him, McCoy, and Hildebrand,[8] is given, and except in the case of *p*-nitrophenol where the ratio of the mean value[9] (excluding Bader's) derived from the various conductivity investigations to 0.83 (the value of γ at 0.1 normal) is adopted. In the case of the basic indicators, the value given is that which the constant would have if the indicator were regarded as an acid.

TABLE 3.—IONIZATION-CONSTANTS OF INDICATORS.

Dimethylaminoazobenzene...	7×10^{-4}	Alizarin..................	9×10^{-9}
Methyl orange..............	5×10^{-4}	Cyanin....................	2×10^{-9}
p-Nitrophenol.	9×10^{-8}	Phenolphthalein...........	2×10^{-10}
Rosolic acid	1×10^{-8}		

It is to be borne in mind that it is not the ionization-constant itself, but the product obtained by multiplying it by $(1 - \alpha)/\alpha$, where α is the fraction of the indicator transformed into its salt at the end-point, that is directly involved in the applications of the theory to volumetric analysis. It is therefore important to know also the limits between which the fraction transformed and therefore this product, designated throughout this article the indicator-function k, can in practice be varied, by adding different quantities of the indicator. In accordance with the considerations of Section 5 and the experiments communicated in the foot-notes thereto, the following values may be provisionally given as representing

[1] *Am. Chem. J.*, 31, 503 (1904).

[2] *Z. Elektrochem.*, 14, 351 (1908).

[3] *Ibid.*, 14, 510 (1904).

[4] *Z. physik. Chem.*, 6, 297 (1890).

[5] *Ber.*, 32, 3070 (1899).

[6] *Rec. trav. chim. Pays. Bas*, 21, 444 (1902).

[7] *J. chim. physique*, 5, 586 (1907).

[8] Salm's value is 8×10^{-10}, McCoy's 0.8×10^{-10}, Hildebrand's 1.7×10^{-10}, and Wegscheider's 1.8×10^{-10}. This disagreement illustrates the uncertainty which is probably attached to the other values obtained by the Salm method, which involved electromotive-force measurements with hydrogen-gas cells.

[9] The separate values are 12×10^{-8} (Bader), 9.6×10^{-8} (Hantzsch), 6.5×10^{-8} (Holleman), and 7.0×10^{-8} (Lundén).

roughly the values of the indicator-function k practically attainable with certain indicators.

TABLE 4.—PROVISIONAL VALUES OF THE INDICATOR-FUNCTION ATTAINABLE WITH VARIOUS INDICATORS.

Dimethylaminoazobenzene: 0.1 K_I or 7×10^{-5}.
Methyl orange: 0.1 K_I or 5×10^{-5}.
p-Nitrophenol: 1000 K_I to $3K_I$ or 9×10^{-5} to 3×10^{-7}.
Phenolphthalein: $20K_I$ to $3K_I$ or 4×10^{-9} to 6×10^{-10}.

26. *Values of the Ionization-Constants of Acids and Bases.*—To facilitate the application of the principles and formulas derived in this article to actual titrations, the ionization-constants of most of the important inorganic acids and bases at or near 25° have been brought together in the following table, and references to summaries of those of the organic acids and bases are given below.

TABLE 5.—IONIZATION-CONSTANTS OF INORGANIC ACIDS AND BASES.

Monobasic acids.	K_A.	Polybasic acids.*	K_{A_1}.	K_{A_2}.*
HCl, HBr, HI.	1	H_2SO_4[6]	1	3×10^{-2}
HNO_3, $HClO_3$, $HClO_4$.....	1	H_2CrO_4[7]	1	6×10^{-7}
HNO_2[1]..................	5×10^{-4}	H_2SO_3[8]	1.7×10^{-2}	.....
HClO[2]........	4×10^{-8}	H_3PO_4[9]	1.1×10^{-2}	2×10^{-7}
HCN[3]..........	7×10^{-10}	H_3AsO_4[10]	5×10^{-3}	.....
HH_2BO_3[4]................	7×10^{-10}	H_2CO_3[8] [11]	3.0×10^{-7}	3×10^{-11}
HH_2AsO_3[5]...............	6×10^{-10}	H_2S[12]	9.1×10^{-8}	1×10^{-15}

Monacidic bases.	K_B.
KOH, NaOH..............................	1
$(\frac{1}{2}Ba)OH$, $(\frac{1}{2}Ca)OH$[13].........	0.3
NH_4OH..................................	1.8×10^{-5}

* K_{A_1} = ionization-constant for the first hydrogen, K_{A_2} = that for the second hydrogen.

[1] Schumann, *Ber.*, 33, 582 (1900); Blanchard, *Z. physik. Chem.*, 41, 706 (1902); Bauer, *Ibid.*, 56, 220 (1906).

[2] Sand, *Z. physik. Chem.*, 48, 614 (1904).

[3] Walker, *Ibid.*, 32, 137 (1900); Madsen, *Ibid.*, 36, 293 (1901).

[4] Lundén, *J. chim. physique*, 5, 580 (1907).

[5] Wood, *J. Chem. Soc.*, 93, 411 (1908).

[6] Noyes and Eastman, *Carnegie Institution Publications*, 63, 274 (1907).

[7] Sherrill, THIS JOURNAL, 29, 1673 (1907). In the case of H_2CrO_4 the relations are somewhat complicated by the fact that the $HCrO_4^-$ ion goes over partly into Cr_2O_7 by dehydration.

[8] Kerp, *Chem. Abstracts*, 4, 442 (1910); Drucker, *Z. physik. Chem.*, 49, 581 (1904).

[9] Abbott and Bray, THIS JOURNAL, 31, 760 (1909). K_{A_3} for H_3PO_4 = 3.6×10^{-13}.

[10] Luther, *Z. Elektrochem.*, 13, 297 (1907).

[11] Bodländer, *Z. physik. Chem.*, 35, 23 (1900); McCoy, *Am. Chem. J.*, 29, 455 (1903).

[12] Auerbach, *Z. physik. Chem.*, 49, 220 (1904); Knox, *Trans. Faraday Soc.*, 1908, 43.

[13] Since barium and calcium hydroxides, like the tri-ionic salts, apparently do not dissociate in stages with formation of the intermediate ions $BaOH^+$ or $CaOH^+$, they can be regarded as monacidic bases.

A comprehensive list of the ionization-constants for organic monobasic acids, for the first hydrogen of organic polybasic acids, and for organic monacidic bases, is given in Kohlrausch and Holborn's "Leitvermögen der Electrolyte" (pp. 176–94); and a more nearly complete one will be found in Lundén's monograph on "Affinitäts-messungen an schwachen Säuren und Basen" (pp. 81–102) in Ahrens' *Sammlung chemischer und chemisch-technischer Vorträge.* Values for the specific acids and bases will also be found under them in Beilstein's and in Meyer and Jacobson's "Handbücher der organischen Chemie." The facts must not, however, be overlooked that the values given in all these books except Lundén's are 100 times the true ionization-constants, which have been employed throughout this article; and that in the case of dibasic acids the values given are ordinarily those for the first hydrogen, while it is those for the second hydrogen that are involved when the total acid is to be titrated. Values for the constants for the second hydrogen of many dibasic acids will be found in an article in THIS JOURNAL by Chandler.[1]

With the aid of Table 2, given near the end of the summary, and the data presented or referred to in this section and the preceding one, the conditions for realizing a satisfactory titration of any particular slightly ionized acid or base may be readily derived; or, if the titration is not practicable, the fact that such is the case may be determined.[2]

BOSTON, May 1910.

---

[1] THIS JOURNAL, 30, 713 (1908).

[2] A concrete example may facilitate the application of these considerations by analysts. Suppose that butyric acid is to be titrated with sodium hydroxide. We find by reference to the summaries of Kohlrausch and Holborn or Lundén or to Meyer and Jacobson's text-book that the ionization-constant K_A for this acid is 1.5×10^{-5}. Referring to the first row of Table 2, we find that the best value of the indicator-function k for the titration of a monobasic acid by a largely ionized base is equal to $10K_WK_A$; therefore for this acid at 25° where $K_W = 10^{-14}$, it is $10 \times 10^{-14} \times 1.5 \times 10^{-5}$ or 1.2×10^{-9}. Reference to Table 3, in Section 25, shows that this value may be secured by using phenolphthalein (for which K_I is 2×10^{-10}) and causing it to be about 14 per cent. transformed into its salt at the end-point (since $k = K_I(1 - \alpha)/\alpha = 2 \times 10^{-10} \times 0.86/0.14 = 1.2 \times 10^{-9}$), and reference to Table 4 in Section 25 shows that it is practicable to secure with phenolphthalein this fraction transformed (since it corresponds to a value of k equal to $6K_I$).

The succeeding expressions in the first row of Table 2 show also that the maximum and minimum values which the indicator-function must have, if an accuracy ρ is to be secured, are $K_A\rho$ and $10K_w/\rho$, respectively; so that in this case if an accuracy of 0.1 per cent. ($\rho = 0.001$) is to be secured, the value of the indicator-function must be between the limits 1.5×10^{-8} and 10^{-10}. This shows that the attained value of the indicator-function must not be greater than 10 times the best value just calculated or smaller than one-tenth of that best value.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 49.]

THE THEORY OF THE DETERMINATION OF TRANSFERENCE NUMBERS BY THE METHOD OF MOVING BOUNDARIES.

BY GILBERT N. LEWIS.

Received May 2, 1910.

In spite of the very important rôle that the transference numbers of electrolytes have played in chemical theory, since Hittorf developed sixty years ago the method of determining these quantities by analysis of the electrode solutions, few really accurate transference numbers have been obtained. This is doubtless due to the very great patience and experimental skill demanded by the Hittorf method. The much simpler method of moving boundaries which was first conceived by Lodge has been so far developed, especially by the recent experiments of Denison and Steele,[1] that it yields results showing a degree of reproducibility rarely attained by the analytical method. It is therefore desirable to subject this method to a careful scrutiny in order to see the precise relation between the transference numbers obtained by its means and those determined by the classical method of Hittorf.

On account of certain discrepancies between the values obtained by the two methods it has frequently been surmised that these differences might be due to the existence of complex ions and that a comparison of the results of the two methods might therefore give some information as to the nature of the ions present in solution. The fallacy of this view has recently been clearly demonstrated by Lash Miller,[2] who emphasizes the fact that the direct method gives transference numbers that, when properly interpreted, are from every point of view identical with those obtained by the analytical determination of the amount of substance transferred from one electrode to the other during electrolysis.

There are, however, two distinct analytical methods of determining transference numbers. In the first, which gives the ordinary or Hittorf transference number, the ratio of the amount of salt to a given amount of water at each electrode is determined before and after electrolysis. This obviously shows the actual transference of the salt only in case the water itself is not transported by the current. The second method, which gives the so-called "true transference number," was first devised by Nernst,[3] and depends upon the use of some reference substance in solution which does not wander with the current, and with respect to which rather than to the water the salt content at each electrode is determined. The practicability of this method has recently been demonstrated by the experiments of Buchböck[1] on hydrochloric acid and especially by the very accurate investigation of the alkali chlorides by Washburn.[2]

---

[1] Denison and Steele, *Z. physik. Chem.*, 57, 110 (1906). Denison, *Trans. Faraday Soc.*, 5, 165 (1909).

[2] *Z. physik. Chem.*, 69, 436 (1909).

[3] *Göttingen Nachricht*, 56, 86 (1900).

If in any case there is a difference between the true and the Hittorf transference numbers, it is not at once obvious which, if either, of these values may be exactly calculated from the experiments on moving boundaries. For normal sodium and potassium chlorides the true and Hittorf numbers are accurately known and these salts have been investigated by Denison and Steele with the moving boundary method. The transference numbers of the anion obtained by the three methods are given in the following table:

	Hittorf.[3]	True [3]	D. and S.
KCl (normal)	0.515	0.505	0.508
NaCl (normal)......	0.631	0 613	0.614

The close agreement between the true transference numbers and those obtained by Denison and Steele was observed by Washburn, and led him to conclude that the method of moving boundaries gives immediately the true transference numbers. This view moreover has been accepted by Denison in a recent paper.[4]

We shall see, however, that the agreement is entirely accidental, and is due to the neglect of a correction which must always be made when the method of moving boundaries is employed, and which, although never entirely ignored by previous writers, has hitherto been neglected in practice. In order to show the nature and magnitude of this correction let us consider the accompanying figure, which represents (diagrammatically) the conditions of Denison and Steele's experiments. The apparatus consists essentially of two electrode chambers, a straight tube AB, and two small tubes E and F into which the liquid rises to a certain height. Assume that the transference number of normal sodium chloride solution is sought A column of this solution is introduced into the center tube, and bounded by two solutions in one of which (LiCl) the cation has a smaller mobility than the sodium ion, and in the other of which ($NaC_2H_3O_2$) the anion has a smaller mobility than the chloride ion. Under these circumstances a current sent through the cell, in the direction shown by the arrows, sharpens the boundaries A and B and causes them to move in opposite directions, say to A′ and B′. Denison and Steele would now consider AA′ proportional to the mobility of sodium, and BB′ to that of chlorine, whence $\frac{AA'}{AA' + B'B}$ and $\frac{B'B}{AA' + B'B}$ are the transference numbers of cation and anion respectively.

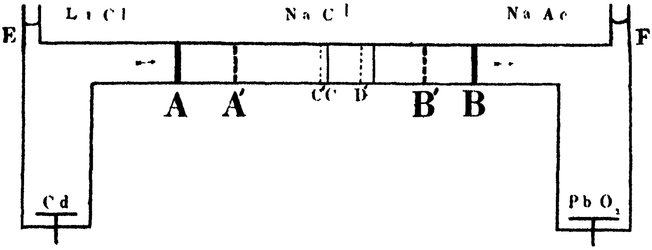
---

[1] *Z. physik. Chem.*, 55, 563 (1906).

[2] *Technology Quart.*, 21, 288 (1908); THIS JOURNAL, 31, 322 (1909); *Z. physik. Chem.*, 66, 513 (1909).

[3] These values for the normal solutions have been obtained by interpolating between the values obtained by Washburn for 1.25 *N* solutions and the accepted values at infinite dilution.

[4] *Trans. Faraday Soc.*, 5, 165 (1909).



The positions and motions of the boundaries are referred to marks on the glass tube or read by a telescope which is stationary with respect to the apparatus, and it is therefore obvious that any flow of the solution bodily through the tube would vitiate the results. Thus if during the experiment liquid were poured into the tube F and allowed to flow out at E, the boundary B would move more and the boundary A less than before, and entirely different transference numbers would be obtained. A like effect would be produced if the tube F were closed, and hydrogen gas evolved at the cathode. Here also there would be a considerable flow of solution through the middle portion of the apparatus. This is of course an extreme case and it is not difficult to find electrodes which permit no evolution of gas. Nevertheless there will always be a certain volume change at each electrode, and therefore to each of Denison and Steele's transference numbers a correction must be applied which depends both upon the salt investigated and upon the kind of electrode used.[1]

In order to illustrate the mode of calculation of this correction and to obtain an idea of its order of magnitude, let us determine the volume changes at each electrode in a typical experiment of Denison and Steele's, in which a normal solution of sodium chloride is electrolyzed with a cadmium anode and a cathode composed of a paste of lead and lead peroxide. Assume now that the tube E in the apparatus is closed and the tube F is open, and that one faraday of electricity passes, whereby the sodium boundary moves from the point A (on the glass tube) to the point A′ and the chloride boundary from B to B′. The solution between A′ and B′ will remain unchanged. Now let C be the original position of what we may call an *average* water particle, and CC′ the change in position of this particle due to flow of liquid caused by a volume change at the cadmium electrode; or, if this idea of the average water particle seems too indefinite, let C and C′ be two points such that there is the same amount of water to the left of C′ after the experiment as there was to the left of C at the beginning. It will now be obvious from our definition that if we measure the positions of A and B from the point C and the positions A′ and B′ from the point C′ we shall be referring the transference of salt to a given quantity of water[1] and thus obtain exactly the Hittorf transference numbers, which are, for the cation, $N_C = \frac{AA' + C'C}{AA' + B'B}$ and for the anion, $N_A = \frac{B'B - C'C}{AA' = B'B}$.

---

[1] The transference numbers obtained from moving boundaries without this correction are analogous to those obtained by the Hittorf method when the amounts of salt transported are referred, not to given weight of water, but, incorrectly, to the contents of a given volume of the apparatus.

To calculate the distance C′C, when one faraday passes, we must find the volume change occurring during electrolysis to the left of our "average water particle." In this calculation we may use a principle which, although not absolutely correct, is sufficiently so for our present purpose. This principle states that the volume of an aqueous solution differs from the volume of pure water which it contains, by a quantity that is proportional to the number of equivalents of the solute present. The proportionality constant is called the apparent equivalent volume of the solute. Thus in the present case the distribution of lithium chloride is changed by the electrolysis, since its concentration between A and A′ will in general be different from that immediately to the left of A.[2] But the total amount of lithium chloride in the portion to the left of C will be unchanged and the volume therefore due to lithium chloride will remain unchanged. The only changes that will affect the volume considered are (1) the disappearance of one equivalent of metallic cadmium, which occupied 6.5 cc.;[3] (2) the formation of one equivalent of cadmium chloride in solution where it has the apparent volume of 12.0 cc.; and (3) the loss of N_C equivalent of sodium chloride, N_C being the Hittorf transference number, for the cation, of sodium chloride. We have given above the value of N_C for normal sodium chloride as about 0.37. The apparent equivalent volume of this salt is 18.0 cc. The total increase of volume, which is the volume between C and C′, is then $12.0 - 6.5 - (0.37 \times 18.0) = -1.2$ cc.

If now the tube E is open and F closed, the flow through the tube is determined by the volume changes in the right-hand portion of the apparatus. Here one equivalent each of lead peroxide (6.7 cc.) and of water (9.0 cc.), and N_A (=0.63) equivalents of sodium chloride with apparent equivalent volume 18.0 cc. have disappeared, one each of lead (4.6 cc.) and sodium hydroxide (—4.1 cc.) have been formed.[1] The total increase in volume is therefore $4.6 - 4.1 - 6.7 - 9.0 - (0.63 \times 18) = -26.6$ cc. In the previous case, where the tube E was closed, we found the volume change hardly greater than the probable error of the calculation, but in the present case, with F closed, the change of 26.6 cc. means a very considerable flow of solution through the tube from left to right.

---

[1] See also Lash Miller, *Loc. cit.*

[2] See Kohlrausch, *Ann. d. Physik*, 62, 237 (1897).

[3] All data concerning equivalent volumes are taken or calculated from the tables of Landolt and Börnstein.

As a matter of fact Denison and Steele left both E and F open. This complicates the matter, but if we assume that both tubes were of the same diameter, then, since the solutions in the two tubes have about the same density, the volume change will be distributed evenly, and the flow of solution will be the mean of the two values we have just calculated, 1.2 in one direction and 26.6 in the other. This is 12.7 cc. or in round numbers 13 cc. flow from left to right.

We have seen that the Hittorf transference numbers are to be calculated by the equations $N_C = \frac{AA' + C'C}{AA' + B'B}$, $N_A = \frac{B'B - C'C}{AA' + B'B}$ while the Denison and Steele transference numbers, which we may represent by N'_C and N'_A are $\frac{AA'}{AA' + B'B}$ and $\frac{B'B}{AA' + B'B}$. Hence $N_A = N'_A - \frac{C'C}{AA' + B'B}$. Now since the tube A B has a uniform bore the quantities AA′, B′B, C′C may represent volumes as well as distances. We will replace C′C then by v, which will denote the total flow of olution from cathode to anode when one faraday passes. It is obvious that AA′ + B′B, the total distance moved by both boundaries during the passage of one faraday, is simply equal to the volume containing one equivalent of salt, which is the reciprocal of the equivalent concentration, c. The above equation therefore becomes,

$$N_A = N'_A - vc.$$

In the above case of normal sodium chloride, $c = 1$, $v = -0.013$ (in liters), N'_A was found to be 0.614, hence N_A, the Hittorf number obtained from Denison and Steele's value, is 0.627.

In the case of normal potassium chloride we may make a similar calculation. Here N_A is about 0.51 and the apparent equivalent volumes are 28.5 cc. for potassium chloride and 6.6 cc. for potassium hydroxide. Proceeding as before we find that the increase of volume is —8.3 cc.

---

[1] Denison and Steele added a trace of acetic acid near the cathode and of alkali near the anode. These substances, if present at the electrodes, would make the reactions somewhat different from those given above. It seems, however, most probable that these substances were used up in the immediate neighborhood of the electrodes by the preliminary current which was always passed through before the readings were begun, and I have assumed this to be the case.

on the left side, and —18.3 cc. on the right. Assuming again that tubes E and F are both open and of the same size, the flow of liquid, v, through the apparatus amounts to —5.0 cc., that is, in the same direction as for sodium chloride. We must therefore add 0.005 to Denison and Steele's value to find the Hittorf transference number for the anion, and thus obtain 0.513 for the latter.

These two transference numbers, 0.627 for normal sodium chloride, and 0.513 for normal potassium chloride obtained by the moving boundary method are close to those found by the analytic method, namely 0.631 and 0.515.

The uncertainty as to the exact conditions of Denison and Steele's experiments makes it impossible to go further into these corrections; but we see at least that they are so large as to render it necessary in the future to carry out moving boundary experiments in such a way that the flow of liquid through the apparatus may be exactly determined. In general it would seem advisable that only one of the tubes, represented by E and F in our figure, be open at a time. The calculation of the correction would then be simplified. Moreover successive experiments with E open and with F open would give independent data, and thus furnish a mutual check. It would also be well to measure the total volume change in the apparatus after the passage of a given amount of current and compare with the calculated.

Denison and Steele found that their transference numbers were much nearer those obtained by the Hittorf method, when they passed from normal to tenth normal solutions. The reason for this is evident from our equation,

$$N_A = N'_A - vc.$$

Since the quantity v is nearly independent of the concentration, the difference between the Denison and Steele and the Hittorf numbers is only one-tenth as great in tenth normal as in normal solutions. Nevertheless the difference even in tenth normal solution may in some cases amount to 1 per cent. or more, and in most cases is larger than the apparent experimental error of the moving boundary method.

So far we have made no assumption concerning the hydration of the ions, and our conclusions are equally valid whether or not water is itself carried with the current. But suppose now that in that portion of the apparatus lying between A and B there is present in solution a small amount of a non-electrolyte which is known not to migrate with the current, and let this substance extend to the point D where its boundary is recognizable by optical methods, or otherwise. Assume that the ions of the electrolyte under investigation are hydrated and that more water is carried by the cation than by the anion. As a result water will be carried during electrolysis, through the non-electrolyte, towards the cathode, and while the point C, which we have defined above, moves to C′, the boundary D will move a greater distance to D′. A little consideration will show that the difference between the volumes C′C and D′D is a direct measure of the volume of water carried by the current, and furthermore that the *true* transference numbers of the electrolyte are given at once by the expressions, $\frac{AA' + D'D}{AA' + B'B}$ for the cation, and $\frac{B'B - D'D}{AA' + B'B}$ for the anion. In this case it is not even necessary to calculate the volume changes at the electrodes, for these are measured directly by the movements of the boundary D.

The only experimental difficulty in such an experiment as we have just proposed would be found in keeping the boundary D sufficiently sharp for accurate reading; for this boundary is not automatically sharpened by the electrolysis as in the case of the boundaries A and B. The difficulty seems, however, by no means insurmountable and this device should furnish a very simple method of investigating ionic hydration, and true transference numbers.[1]

We have seen that the analytical method of Hittorf is capable of yielding the true transference numbers when a stationary non-electrolyte is employed, as in the experiments of Buchböck and Washburn. Another familiar method of obtaining transference numbers consists in the determination of the electromotive force of cells with and without transference. I have shown in another place[2] that by the use of a stationary non-electrolyte it is possible to determine ionic hydrations and thus true transference numbers. These methods together with the one outlined above suggest that any method of determining the Hittorf transference numbers may with some modification be made to yield true transference numbers, but only by the employment of a non-electrolyte which does not migrate with the current.

Summary.

It is shown that the transference numbers of Denison and Steele are subject to a considerable correction on account of volume changes at the electrodes, the correction being larger, the more concentrated the solution. When this correction is applied the method of moving boundaries gives, theoretically and practically, the Hittorf transference numbers, and not the true transference numbers.

---

[1] Evidently when the amount of water carried by the current has been determined by some other method the true transference number may be obtained directly from the Denison and Steele values. It is to be noted that either the true or the Hittorf number is obtained from Denison and Steele's by making a correction for the volume changes at the electrodes. In the first case the volume change includes the volume of the water carried, in the second case it does not.

[2] THIS JOURNAL, 30, 1355 (1908); *Z. Elektrochem.*, 14, 509 (1908).

A method is proposed for obtaining true transference numbers from moving boundary experiments through the aid of a non-electrolyte which does not migrate with the current.

BOSTON, MASS., April 16, 1910

THE PHOSPHATES OF CALCIUM. IV.[1]

BY FRANK K. CAMERON AND JAMES M. BELL.

Received May 12, 1910

Owing to the increasing importance of the phosphates of calcium in the fertilizer industry, a knowledge of their behavior in water and in solutions becomes increasingly important. Some years ago two papers[2] were published from this laboratory, in which it was shown that at 25° the solutions, resulting from the mixture of the phosphates of calcium with water, always contain a greater ratio of P_2O_5/CaO than does the original solid. Thus the effects observed are not merely solubility effects but there is also an hydrolysis. So, each of the phosphates of calcium may exist in equilibrium with a series of solutions, in which the ratios of P_2O_5/H_2O and CaO/H_2O vary between rather wide limits.

It was found that at 25° solid monocalcium phosphate could exist in equilibrium with solutions containing over 320 grams phosphoric anhydride per liter. Below this concentration the stable solid was dicalcium phosphate. In the former analyses of these solids, only the ratio P_2O_5/CaO was determined, no estimation having been made of the amount of water of crystallization. The solids analyzed were always contaminated with the adhering mother liquor. In the determination of the above ratio this contamination is not a very serious source of error, as the mother liquor was present in small quantity compared with the crystals, and as the mother liquor was always much poorer both in phosphoric anhydride and in calcium oxide than were the crystals. Further, any determination of the amount of water would have been subject to an enormous error, as the percentage of water in the crystals is small, and that in the adhering liquid was very large. Consequently, the composition of the solid phase was taken as $CaHPO_4.2H_2O$, the ordinary dihydrate of dicalcium phosphate.

That this assumption seemed to be confirmed was indicated in a paper published subsequently by Bassett.[3] In this paper it was announced that above 30° the solid dicalcium phosphate dihydrate changed into the anhydrous salt. At 30° there is an invariant point, the five phases being the two forms of dicalcium phosphate (anhydrous and dihydrate), monocalcium phosphate monohydrate, solution and vapor. Also it was announced that 80° was the maximum temperature at which the dihydrate could exist, the five phases being the two hydrates of dicalcium phosphate, tricalcium phosphate, solution and vapor. Under these conditions there is a transition interval for the reaction

---

[1] Published by permission of the Secretary of Agriculture.

[2] Cameron, Seidell and Bell, THIS JOURNAL, 27, 1503, 1512 (1905).

[3] *Z. anorg. Chem.*, 53, 34 (1907).

$$CaHPO_4.2H_2O \rightleftarrows CaHPO_4 + \text{solution}$$

between 30° and 80°. Thus according to this publication the stable hydrate of dicalcium phosphate below 30° was the dihydrate, or possibly some higher hydrate.

Later Bassett[1] corrected his early temperature measurements, this transition interval being given as from 21° to 36°. This work would indicate that at 25° the anhydrous salt would be the stable form in equilibrium with the more concentrated solutions. And, as the temperature 25° is nearer 21° than 36°, it would be supposed that the dihydrate would exist over a much greater range of concentration than does the anhydrous salt. This supposition is, however, not confirmed by Bassett's results at 25°, for he finds that $CaHPO_4.2H_2O$ exists in equilibrium with solutions *below* 0.5 per cent. phosphoric anhydride. Above this value up to 23 per cent. phosphoric anhydride in solution, the solid phase is $CaHPO_4$. Thus the transformation at 25°

$$CaHPO_4.2H_2O \rightleftarrows CaHPO_4 + 2H_2O$$

has the same vapor pressure as an aqueous solution containing approximately 0.5 per cent. phosphoric anhydride and 0.2 per cent. lime. It is obvious that this vapor pressure cannot be much below that of pure water. This result does not appear to be in accord with the following statement of Bassett.[2] "Ein solcher Versuch wurde begonnen, gab aber kein Resultat *wegen des ausserordentlich geringen Wasserdampfdruckes von* $CaHPO_4.2H_2O$."[3]

Owing to the confusion regarding the relative stability of the hydrated and the anhydrous dicalcium phosphate, the following experiments were made at 25°. Solutions of phosphoric acid of varying concentration were prepared, the total volume of these solutions being 180 cc. To each mixture weighed quantities of potassium chloride (about 5 grams) were added and Kahlbaum's tricalcium phosphate in sufficient quantity to give a permanent precipitate. The reasons for the addition of potassium chloride should be further explained. As has been stated above, an analysis of the solid phase with the adhering mother liquor is useless to determine the water present in a solid. Also, the residue method of Schreinemakers[4] and Bancroft[5] fails, because the line joining the two points (representing $CaHPO_4.2H_2O$ and $CaHPO_4$) is almost parallel with the tie lines, and consequently very slight errors of analysis of the solution or of the solid residue might give erroneous results regarding the composition of the solid phase. A modification of this method, the "tell-tale" method,[1] was employed. This differs from the method of residues in this way. By the method of residues lines joining the points representing solution and residue are joined and produced. Where three or more such lines pass through a point, the point represents the composition of the solid phase. By the "tell-tale" method, it becomes possible to calculate the quantity of liquid adhering to the crystals, and consequently to calculate how far to produce this tie line. Where the different tie lines met at a large angle, the first method has been used generally, but where tie lines meet at a very small angle, the second method is to be preferred. One condition to be fulfilled in this latter case, is that the "tell-tale" substance must be present only in the liquid phase. That the condition was satisfied here was indicated by the analysis of the liquid phase, for almost exactly the calculated quantity of chloride was found per unit of solution. Consequently this quantity is a measure of the quantity of solution adhering to the solid. Also from an analysis of the liquid the quantity of all the components present in the adhering liquid may be estimated. By subtracting these from the quantities found by analysis in the total residue, the composition of the solid may be found. In every case the quantity of water was determined by difference and so all the errors of experiment are heaped on these values. In spite of the fact that a slight error in the chloride determinations is multiplied many times in the corresponding quantities of water and that the water in the solid is the difference between two large values, the results by this method give fairly concordant values for the composition of the solid phases. The following table gives the results of the analyses:

---

[1] *Z. anorg. Chem.*, 59, 1 (1908).

[2] *Loc. cit.*, p. 40.

[3] The italics are ours.

[4] *Z. physik. Chem.*, 11, 81 (1893).

[5] *J. Physic. Chem.*, 6, 178 (1902).

TABLE.

	Solution.					Residue.				
No	Total	CaO.	P_2O_5.	KCl.	H_2O	Total	CaO	P_2O_5	KCl	H_2O.
112	25 014	0 052	0.152	0.685	24.125	9.162	1 934	2.336	0 099	4.793
115	24.528	0 103	0.290	0.659	23.476	10.531	2.439	3.033	0 091	4 968
119	26 196	0 249	0.685	0.703	24.559	8.463	1 609	2 054	0.102	4 698
122	15.701	0.252	0.741	0.409	14.299	7 278	1 774	2.271	0 053	3.180
126	5.469	0.161	0.500	0.134	4.674	11.627	2 719	3 561	0.094	5.253
127	3.656	0 158	0 585	0 090	2.823	21.495	5 745	8 134	0.189	7.427
130	5.254	0.287	1 355	0.106	3 506	14 797	2 095	6 051	0.157	6.494

The calculations of the compositions of the solid phase for one mixture (No. 126) follow. The ratios of the components in the residue, the solution and the solid are as follows:

---

[1] Bancroft, *J. Physic. Chem.*, 9, 558 (1905); later called the "tell-tale" method by Kenrick, *J. Physic. Chem.*, 12, 693 (1908).

	KCl.	CaO.	P_2O_5.	H_2O.
Residue	1	28.93	37.87	55.88
Solution	1	1.20	3.73	34.88
Solid	.	27.73	34.14	21.00

The values for the solid are the differences between the corresponding values for the solution and residue. In molecular ratios the values for the solid are

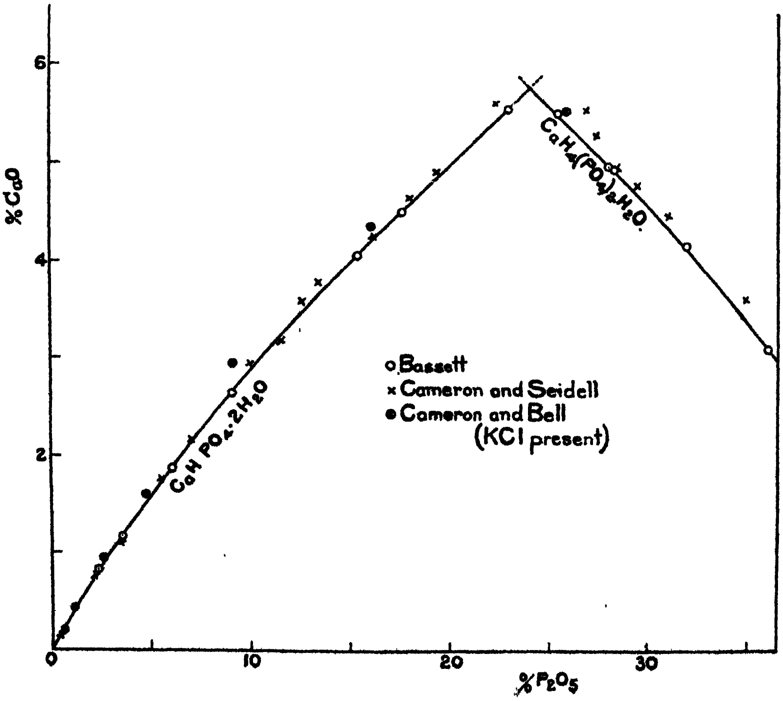
$$2.06\ CaO : 1.00\ P_2O_5 : 4.86\ H_2O.$$

The following table gives the molecular ratios calculated similarly for the solids in each of the other mixtures:

TABLE.

No.	CaO.	P_2O_5	H_2O.	Composition of solids.
112	2.11	1	4.39	
115	1.94	1	4.51	$2CaO.P_2O_5.5H_2O$ or $CaHPO_4.2H_2O$
119	2.03	1	4.66	
122	2.02	1	4.78	
126	2.06	1	4.86	
127	1.99	1	1.72	
130	1.04	1	2.55	$CaO.P_2O_5.3H_2O$ or $CaH_4(PO_4)_2.H_2O$

It is evident from these results that the stable solid phase up to a concentration of about 15 per cent. P_2O_5 is $CaHPO_4.2H_2O$. One result



(No. 127) indicates that there is a lower hydrate of $CaHPO_4$. It is probable that this is the anhydrous salt and that the single point (No. 127) gives the conditions at 25° for the transition

$$CaHPO_4.2H_2O \rightleftarrows CaHPO_4 + 2H_2O.$$

As the KCl present in solution influences the vapor pressure of the solution, concentrations of calcium oxide and phosphoric anhydride in each case are somewhat lower than for the corresponding solution where no potassium chloride is present.

These results also show the effect of potassium chloride in concentrations of about 25–30 grams per liter upon the system $CaO–P_2O_5–H_2O$. In the accompanying diagram are given the results of Bassett, of Cameron and Seidell, and of the present paper where potassium chloride is present. These last results lie above the curves drawn through the former points. Thus the effect of the potassium chloride is to increase the lime in solution.

In this paper it has been shown that:

1. The presence of potassium chloride in solution containing calcium oxide and phosphoric anhydride increases slightly the lime content of solutions in equilibrium with dicalcium phosphate and monocalcium phosphate.

2. By the "tell-tale" method the composition of the solid phases was found to be $CaHPO_4.2H_2O$ and $CaH_4(PO_4)_2.H_2O$ with a region between, which was not explored, where the composition of the solid was probably $CaHPO_4$.

3. This result is in accord with Bassett's last determination of the transition interval of $CaHPO_4.2H_2O \rightleftarrows CaHPO_4 + 2H_2O$ but is not in accord with his direct determination of the compositions of the solid phases.

BUREAU OF SOILS,
U. S. DEPT OF AGRICULTURE,
WASHINGTON, D. C.

BASIC NITRATE OF YTTRIUM.

BY C. JAMES AND L. A. PRATT.

Received May 7, 1910.

Of all the methods that have been published for the separation of yttrium and erbium, the classic procedure of Bahr and Bunsen[1] still serves best. It was therefore considered that a study of the system Y_2O_3, N_2O_5, H_2O would be highly interesting.

The only basic nitrate mentioned by Bahr and Bunsen was given the formula (recalculated) $2Y_2O_3.3N_2O_5.9H_2O$, which was derived from the analysis of the air-dried salt. It is highly probable that their compound was contaminated with normal nitrate from adherent mother liquor.

---

[1] *Ann.*, 137, 1 (1866).

In order to study the system Y_2O_3, N_2O_5, H_2O, it was necessary to prepare a comparatively large amount of pure yttrium oxide, since yttrium nitrate is extremely soluble.

The Preparation of Yttria Material.—The crude yttria earths were first submitted to a long fractional crystallization by the bromate method.[1] By this procedure samarium, gadolinium, terbium, dysprosium and holmium separated in the least soluble portions. The middle fractions contained yttrium, together with a little erbium and holmium, while the most soluble portion carried nearly all the erbium and all the thulium, ytterbium, lutecium and scandium.

The middle fractions were then precipitated as the hydroxide and well washed with boiling water. The hydroxides were next converted into the nitrates and the latter subjected to fractional decomposition. This was carried out by evaporating the solution and fusing until a portion had decomposed. The evolution of red fumes was allowed to proceed until the surface acquired a peculiar steely appearance. This point was easily ascertained by experience. The decomposition was not allowed to continue until the mass became creamy.

In order to find the best method of obtaining the solution of the melt, several plans were tried. It was discovered that the simplest way was to pour the fused mass into cold water. Great care was required in order to prevent spattering. The result of this operation was a nicely granulated product, which rapidly disintegrated upon boiling.

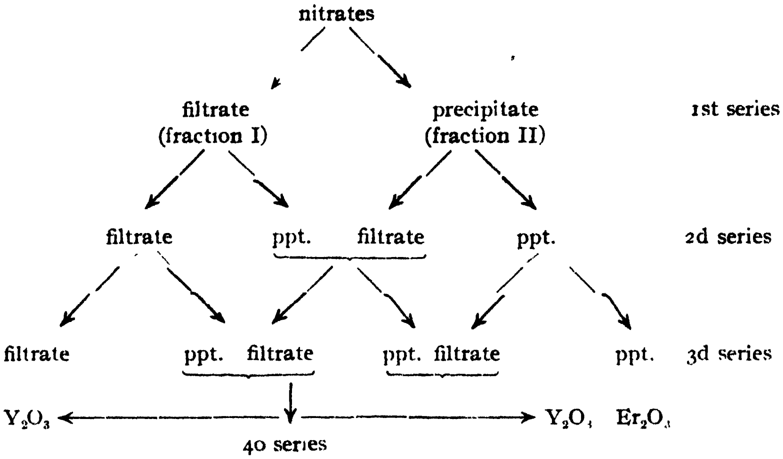
Under the best conditions the entire mass went into solution; especially was this true of the yttrium end of the series. Upon cooling, the basic nitrates separated out in a crystalline form. At the opposite end—the least basic portion—of the fractions there always remained an insoluble basic nitrate, unless the decomposition was stopped at an earlier stage, *i. e.*, when there was a copious evolution of red fumes.

In case a precipitate remained, it was highly important that it should be well agitated by thorough boiling. After cooling, the precipitate was filtered off (Fraction II), redissolved in nitric acid and again fused. The filtrate (Fraction I) was also boiled down, and fused. This second series gives two filtrates and two precipitates. The filtrate from Fraction II was mixed with the precipitate from Fraction I with the result that the second series contained three fractions. The diagram below will readily show the manner in which the work was carried out.

About 40 series of operations were carried out, yielding two kilos of yttrium nitrate. The nitrate was dissolved in water, heated and precipitated by means of oxalic acid. The resulting oxalate was filtered off, well washed, dried and ignited.

---

[1] THIS JOURNAL, 30, 182.



The white oxide obtained in this way was dissolved in an excess of nitric acid, and twice crystallized from this solvent.

A saturated solution of the nitrate was then prepared by using 1 kilogram of the salt. The spectroscope showed only very faint bands of erbium and holmium when viewed through a layer 12.5 cm. thick and the solution was perfectly colorless. Therefore, it was considered sufficiently pure for the study of the basic nitrates.

Some of the remaining fractions of yttrium, which still contained a little erbium and holmium, were put through a modified chromate method. This yielded a further supply of yttrium oxide of such a purity that, when converted into a concentrated solution of the nitrate, it showed no absorption bands through a layer of about 5 cm.

Twenty-two solutions were prepared, in regularly increasing concentrations of yttrium nitrate, from great dilution to a saturated solution. These solutions together with an excess of yttrium oxide were placed in bottles of 100 cc. capacity, and rotated in a thermostat at 25°. After an interval of three months, several of the solutions were analyzed. During the analysis, it was observed that the solid phase, in those solutions having a fairly high concentration of yttrium nitrate, was composed of fine crystals. These bottles cleared in a comparatively short time so that the supernatant liquid could be readily drawn off. In the bottles, where the concentrations were not so great, the solid phases settled with difficulty, and had more the appearance of a hydroxide. After four and a half months of rotation, the system was found to be in equilibrium. The solutions were withdrawn, and the yttrium, present as the hydroxide and the total yttrium determined.

Several difficulties were encountered in carrying out these analyses, and different methods were tried in order to reduce errors to a minimum. The following methods gave the most accurate and rapid results:

A weighed amount of mother liquor was, after considerable dilution, titrated to the neutral point with standard nitric acid (approximately $^1/_{10}$ normal) using methyl orange as the indicator. From this, the amount of yttrium oxide, present as hydroxide, was easily calculated. Checks, which were run on several of the solutions, proved that dependence could be placed upon the results obtained.

In order to determine the total yttrium, the solutions, which had previously been titrated, were diluted to 200 cc. Aliquot portions of these diluted solutions were warmed, and treated with a slight excess of an oxalic acid solution. After being allowed to stand for some time, the precipitate was filtered off, dried, and carefully ignited to the oxide in a weighed platinum crucible.

The data obtained from the analyses of the solutions are given in Table I and shown graphically in Fig. 1.

TABLE I.

No.	Density 25°/25°.	Per cent. Y_2O_3 as $Y(NO_3)_3$.	Per cent. Y_2O_3 as $Y(OH)_3$.	Grams $Y(NO_3)_3$ in 100 grams H_2O	Grams Y_2O_3 as $Y(OH)_3$ in 100 grams H_2O
1	1.0260	1.25	0.014	3.13	0.014
2	1.0675	3.17	0.021	8.37	0.022
3	1.1106	5.01	0.033	13.87	0.034
4	1.1506	6.57	0.039	19.05	0.048
5	1.1907	8.20	0.049	24.94	0.063
6	1.2350	9.58	0.071	30.46	0.091
7	1.2517	10.19	0.121	33.02	0.160
8	1.2897	11.45	0.088	38.71	0.122
9	1.3268	12.61	0.079	44.35	0.114
10	1.3698	14.02	0.068	51.87	0.103
11	1.4104	15.17	0.060	58.61	0.095
12	1.4484	16.31	0.054	65.89	0.090
13	1.4867	17.33	0.045	73.03	0.078
14	1.5231	18.33	0.039	80.67	0.072
15	1.5587	19.34	0.039	89.06	0.074
16	1.5923	20.10	0.038	95.98	0.074
17	1.6259	20.91	0.037	103.80	0.075
18	1.6603	21.82	0.037	113.40	0.079
19	1.6931	22.59	0.036	122.40	0.080
20	1.7260	23.37	0.032[1]	132.10	0.074
21	1.7440	23.74	0.035	137.10	0.083
22	1.7446	2[illegible].07	..	141.60	

Bottle No. 21 contained an excess of both basic yttrium nitrate and yttrium nitrate. Bottle No. 22 contained only an excess of yttrium nitrate, which gave for the solubility of this compound at 25° 141.6 grams per 100 grams of water.

For the analysis of the solid phase, the sample was withdrawn, freed, as far as possible, from adhering mother liquor, by pressing between filter paper, after which it was quickly transferred to a weighing bottle and carefully mixed. A known amount was then ignited in a weighed platinum crucible for total yttrium. In another portion of the same sample the yttrium oxide as yttrium hydroxide was estimated by dissolving a weighed amount in an excess of standard nitric acid, and titrating back to neutrality with a sodium carbonate solution of known ratio. In this case methyl orange was again used as the indicator.

---

[1] This result undoubtedly contains a slight error, but, unfortunately, the bottle was emptied before it could be checked.

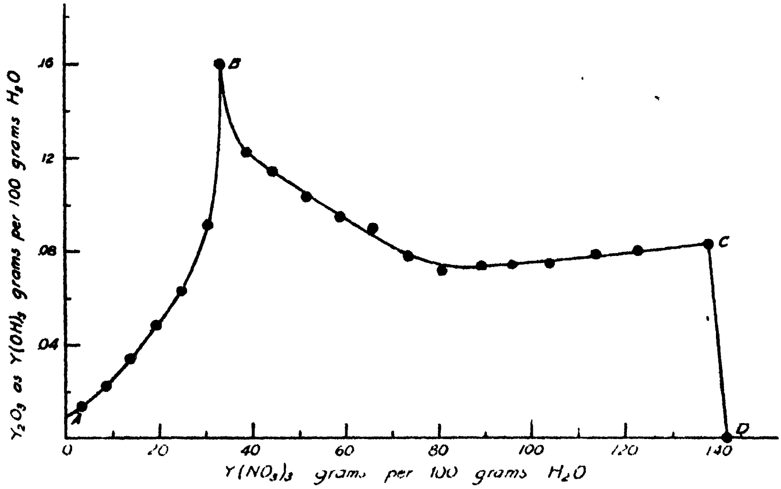


Fig. 1.

The results are given in Table II, and plotted on the triangular diagram in Fig. 2.

TABLE II.

Point.	Solutions.		Point.	Solids.		Bottle No
	Y_2O_3.	N_2O_5.		Y_2O_3.	N_2O_5.	
E	1.26	1.79	E′	49 55	13.29	1
F	3.19	4 55	F′	45.20	12.96	2
G	5.04	7.18	G′	42 97	13.74	3
H	6.61	9.42	H′	47.82	14.56	4
I	9.65	13.74	I′	41.67	16.22	6
J	11.54	16.42	J′	39.78	26.98	8
K	12.69	18.08	K′	38.09	26.93	9
L	15 23	21.75	L′	38.21	27.89	11
M	16.36	23.39	M′	38.39	28.12	12
N	17.38	24.83	N′	38.19	28.70	13
O	18.37	26.28	O′	38.44	29.19	14
P	19.38	27.73	P′	37.83	29.58	15

It will be seen that the lines (EE′, FF′ and GG′, etc., of Fig. 2) joining points represented on curve AB of Fig. 1 do not intersect at a common point; also the solids, upon examination, showed a great resemblance to yttrium hydroxide. Therefore the precipitates along this line can only be solid solutions. Lines joining any points along the curve BC (Fig. 1) meet at a common point x, which corresponds to a definite hydrated basic nitrate of yttrium possessing the formula $3Y_2O_3.4N_2O_5.20H_2O$.

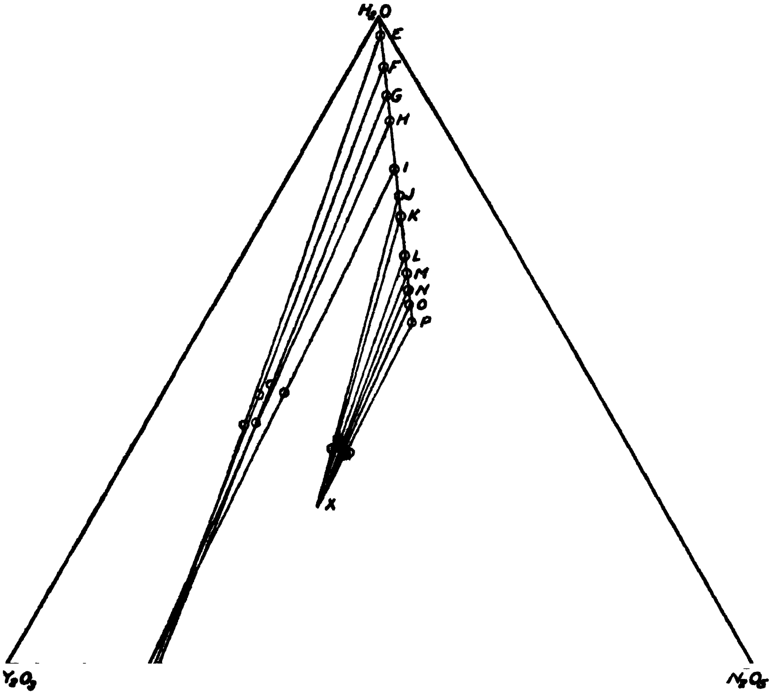


Fig 2.

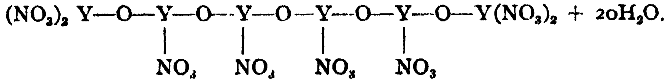
The basic nitrate consisted entirely of small crystals, which were rapidly decomposed by water. The compound, however, was not affected by continued washing with absolute alcohol, and, since the normal nitrate is very soluble in this liquid, it could be entirely separated from the basic nitrate. The solids from several bottles along the curve BC were filtered upon a Hirsch funnel, washed with absolute alcohol, air-dried, and analyzed. The results obtained were as follows:

Calculated	Y_2O_3..............	46.10	N_2O_5.....	29.40	H_2O	24.50
Found (bottle 10)	Y_2O_3..............	46.09	N_2O_5.....	29.55	H_2O (diff.)	24.36
Found (bottle 11)	Y_2O_3..............	45.96	N_2O_5.....	29.67	H_2O (diff.)	24.37
Found (bottle 13)	Y_2O_3..............	45.82	N_2O_5.....	29.67	H_2O (diff.)	24.51

The basic compound from still another bottle was dissolved in yttrium nitrate solution, and recrystallized after filtering. The mother liquor was separated by suction, the crystals washed with absolute alcohol, and air-dried. The analytical results obtained agreed well with the above as may be seen:

Y_2O_3............... 45.82 N_2O_5............. 29.67 H_2O........... 24.51

For this compound the authors offer the following complex formula:



$$(NO_3)_2\,Y{-}O{-}\underset{\overset{|}{NO_3}}{Y}{-}O{-}\underset{\overset{|}{NO_3}}{Y}{-}O{-}\underset{\overset{|}{NO_3}}{Y}{-}O{-}\underset{\overset{|}{NO_3}}{Y}{-}O{-}Y(NO_3)_2 + 20H_2O.$$

From the foregoing work the following conclusions are drawn:

First, that the basic compound mentioned by Bahr and Bunsen does not exist. Their results were undoubtedly due to adherent normal nitrate.

Secondly, the only basic nitrate that does exist at 25° is the one corresponding to the formula $3Y_2O_3.4N_2O_5.20H_2O$.

Thirdly, this compound is stable in air and can exist in contact with water containing more than 33 grams of yttrium nitrate to 100 grams of water.

New Hampshire College,
Durham, N. H.

THE RATE OF EXTRACTION OF PLANT FOOD CONSTITUENTS FROM THE PHOSPHATES OF CALCIUM AND FROM A LOAM SOIL.

By James M. Bell.

Received March 28, 1910.

In a recent paper[1] entitled "Ein Beitrag zur Düngemittel und Bodenanalyse," E. A. Mitscherlich, R. Kunze, K. Celichowski, and E. Merres, have investigated the rate of solution of two phosphates of calcium and the rate of extraction of lime from a loam soil, by water saturated with carbon dioxide. The conclusion was reached that the usual equation expressing the rate of solution does not accord with their data. In this equation, *viz.*:

$$dy/dt = k(A - y) \qquad (1)$$

which when integrated becomes

$$\log (A - y) = \log A - kt \qquad (2)$$

A represents the concentration of the solution when final equilibrium is reached. In applying these equations, however, the authors have mistaken the significance of A; since the value of A used by them was the total quantity of the salt which was originally mixed with the carbonated water, and not that portion of salt which the liquid was capable of dissolving. Only when the quantity of salt added to the water is just sufficient for saturation is the above procedure valid. Since in the experiments, two different original ratios of dicalcium phosphate to water were employed, *viz.*: 1 : 750 and 1 : 1500, at least in one case (and probably in both) a wrong value was assigned to A. In the case of tricalcium phosphate four different ratios of salt to water were employed, *viz.*: 1 : 1500, 1 : 2000, 1 : 3000, and 1 : 6000. So that in three of the four series, and probably also in the fourth, incorrect values were assigned to A.

---

[1] *Landw. Jahrb.*, 39, 299 (1910).

As the above equations under these conditions failed to accord well with the data, a modified form of equation (2) has been proposed by the above authors,

$$\log (A - y) = \log A - ct^n \ldots\ldots\ldots\ldots (3)$$

in which A represents the total quantity of the salt and c and n are constants. It seems to me proper, therefore, to recalculate the results, in order to determine whether equations (1) and (2) are really out of accord with the data.

Before discussing the recalculated results, several features of solution phenomena should be recalled. It is obvious that the rate of solution of any substance depends upon its exposed surface. Where the substance is in grains of widely different sizes, it is not possible to deduce any *rational* equation representing the rate of solution of such an aggregation of particles. And further, if any *empirical* equation is found to conform with the data for material in one mechanical condition, that equation will not, in general, describe the rate of solution of material which is chemically the same but mechanically different. Consequently experiments on rate of solution have usually been carried out with large crystals of low solubility, the surface changing but slightly during the course of the experiment. It is apparent also that an aggregation of crystals of uniform size and of low solubility may be considered as of constant surface during the solution.

In the experiments of Mitscherlich, Kunze, Celichowski, and Merres powdered material was probably used, but no statement is made as to its mechanical condition. The data indicate that the surface exposed must have altered considerably, for in the experiments with dicalcium phosphate over half of the phosphoric anhydride was extracted, and in the experiments with tricalcium phosphate, at least 45 per cent. of the phosphoric anhydride was extracted. Consequently, even if the proper value of A (the total quantity of phosphoric anhydride in solution at equilibrium) had been used in the calculations, the usual equation for rate of solution might have failed because of the great changes in the extent of surface.

In the tables the first figures give the concentration of the solution one hour after the salt and water were mixed. In my recalculated results, this has been taken as the starting point of the reaction, for the following reasons: In every case more phosphoric anhydride passed into solution within the first hour (within which no determinations were made) than in the remaining time of the reaction (23-47 hours). Thus, calculated on the basis of 45.55 per cent. phosphoric anhydride in dicalcium phosphate, in one case the increase was from 20.16 per cent. after 1 hour to only 23.03 per cent. after 47 hours more, and in the other case the variation was between 35.09 per cent. and 39.67 per cent. Similarly for tricalcium phosphate with 43.22 per cent. phosphoric anhydride, the increases for four experiments were as follows: From 14.92 per cent. after 1 hour to 19.83 per cent. after 47 hours more; from 17.24 per cent. after 1 hour to 24.69 per cent. after 24 hours; from 20.99 per cent. after 1 hour to 34.55 per cent. after 48 hours; and from 21.46 per cent. after 1 hour to 42.14 per cent. after 24 hours. Thus, for most of the cases, the solution has been very close to equilibrium, and the extent of surface has probably changed but little. For the last two cases given (Tables V and VI) however, the changes in surface have been considerable. In the recalculated results this surface factor has been assumed constant, a legitimate assumption in all but two cases (Tables V and VI). Even in these two cases, in spite of this objection to the application of the usual equation, it will be seen that the equation describes the facts at least as well as the empirical equation proposed by the above authors.

TABLE I.—RATE OF SOLUTION OF DICALCIUM PHOSPHATE IN WATER SATURATED WITH CO_2. RATIO OF SALT TO WATER, 1 : 750. TEMP. 30° C.

Original.			Recalculated.			
t	y found.	y calc. from eqn. (4).	T $t-1$.	Y $y-20.16$.	Y calc. from eqn. (5).	y calc. Y + 20.16.
1	20.16	20.05	0	0	0	20.16
2	20.80	20.56	1	0.64	0.23	20.39
4	21.15	21.10	3	0.99	0.64	20.80
8	21.42	21.63	7	1.26	1.29	21.45
12	21.53	21.94	11	1.37	1.76	21.92
24	22.78	22.47	23	2.62	2.53	22.69
48	23.03	23.02	47	2.87	2.93	23.09

$$\log (45.55-y) = 1.6585-0.252\sqrt[20]{t} \qquad (4)$$

$$\log (3.00-Y) = \log 3.00-0.035T \qquad (5)$$

TABLE II.—RATE OF SOLUTION OF DICALCIUM PHOSPHATE IN WATER SATURATED WITH CO_2. RATIO OF SALT TO WATER, 1 : 1500. TEMP. 30° C.

Original.			Recalculated.			
t.	y found.	y calc. from eqn. (6)	T = $t-1$.	Y = $y-35.09$	Y calc from eqn. (7).	y calc Y + 35.09.
1	35.09	35.00	0	0	0	35.09
2	35.82	36.05	1	0.73	0.68	35.77
4	37.09	37.06	3	2.00	1.76	36.85
8	38.29	38.02	7	3.20	3.11	38.20
12	38.67	38.56	11	3.58	3.82	38.91
24	39.31	39.45	23	4.22	4.49	39.58
48	39.67	40.21	47	4.58	4.60	39.69

$$\log (45.55-y) = 1.6585-0.635\sqrt[10]{t} \qquad (6)$$

$$\log (4.60-Y) = \log 4.60-0.70T \qquad (7)$$

TABLE III.—RATE OF SOLUTION OF TRICALCIUM PHOSPHATE IN WATER SATURATED WITH CO_2. RATIO OF SALT TO WATER, 1 : 1500. TEMP. 30° C.

Original.			Recalculated.			
t.	*y* found.	*y* calc. from eqn. (8).	T = *t* — 1.	Y = *y* — 14.92.	Y calc. from eqn. (9).	*y* calc. = Y + 14.92.
1	14.92	17.29	0	0	0	14.92
2	16.31	17.78	1	1.39	1.03	15.95
4	18.15	18.23	3	3.23	2.49	17.41
8	18.92	18.71	7	4.00	4.00	18.92
12	18.96	18.99	11	4.04	4.60	19.52
18	19.05	19.27	17	4.13	4.90	19.82
24	19.68	19.48	23	4.76	4.97	19.89
48	19.83	19.97	47	4.91	5.00	19.92

$\log (43.22 - y) = 1.6357 - 0.222 \sqrt[20]{t}$ .... (8)

$\log (5.00 - Y) = \log 5.00 - 0.100T$ .... (9)

TABLE IV.—RATE OF SOLUTION OF TRICALCIUM PHOSPHATE IN WATER SATURATED WITH CO_2. RATIO OF SALT TO WATER, 1 : 2000. TEMP. 30° C.

Original.			Recalculated.			
t.	*y* found.	*y* calc. from eqn. (10)	T = *t* — 1	*y* = *y* — 17.24.	Y calc. from eqn. (11).	*y* calc. = Y + 17.24.
1	17.24	21.51	0	0	0	17.24
2	20.19	22.20	1	2.95	2.19	19.43
4	20.75	22.92	3	5.51	4.84	22.08
8	23.68	23.59	7	6.44	6.83	24.07
12	23.90	24.04	11	6.66	7.33	24.57
24	24.69	24.77	23	7.45	7.50	24.74

$\log (43.22 - y) = 1.6357 - 0.299 \sqrt[16]{t}$ .... (10)

$\log (7.50 - Y) = \log 7.50 - 0.150T$ .... (11)

TABLE V.—RATE OF SOLUTION OF TRICALCIUM PHOSPHATE IN WATER SATURATED WITH CO_2. RATIO OF SALT TO WATER, 1 : 3000. TEMP. 30° C.

Original.			Recalculated.			
t	*y* found.	*y* calc. from eqn. (12).	T = *t* — 1.	Y = *y* — 20.99.	Y calc. from eqn. (13).	*y* calc. = Y + 20.99.
1	20.99	24.78	0	0	0	20.99
2	24.35	26.60	1	3.36	3.19	24.18
4	28.55	28.44	3	7.56	5.60	26.59
8	30.66	30.28	7	9.67	9.67	30.56
12	31.30	31.34	11	10.31	11.46	32.45
24	33.71	33.06	23	12.72	13.01	34.00
48	34.15	34.70	47	13.16	13.20	34.19

$\log (43.22 - y) = 1.6357 - 0.370 \sqrt[6]{t}$ .... (12)

$\log (13.20 - Y) = \log 13.20 - 0.080T$ .... (13)

TABLE VI.—RATE OF SOLUTION OF TRICALCIUM PHOSPHATE IN WATER SATURATED WITH CO_2. RATIO OF SALT TO WATER, 1 : 6000. TEMP. 30° C.

	Original.		Recalculated.			
t.	y found.	y calc. from eqn. (14).	$T = t - 1$.	$Y = y - 21.48$.	Y calc. from eqn. (15).	y calc. = $Y + 21.48$.
1	21.48	28.31	0	0	0	21.48
2	30.30	32.59	1	8.82	6.40	27.88
4	36.71	36.44	3	15.23	13.85	35.33
8	39.67	39.48	7	18.19	19.13	40.61
12	40.88	40.77	11	19.40	20.34	41.82
24	42.14	42.22	23	20.66	20.70	42.18

$$\log (43.22 - y) = 1.6357 - 0.462\sqrt[6]{t^2} \dots\dots \quad (14)$$

$$\log (20.70 - Y) = \log 20.70 - 0.160T \dots\dots \quad (15)$$

TABLE XXI.—RATE OF SOLUTION OF LIME FROM A LOAM SOIL BY WATER SATURATED WITH CO_2. RATIO OF SOIL TO WATER, 1 : 10. TEMP. 30° C.

	Original.		Recalculated.			
t.	y found.	y calc. from eqn. (16)	$T = t - 2$	$Y = y - 0.1087$.	Y calc. from eqn. (17).	y calc. = $Y + 0.1087$.
2	0.1087	0.1069	0	0	0	0.1087
4	0.1199	0.1232	2	0.0112	0.0107	0.1194
8	0.1342	0.1378	6	0.0257	0.0264	0.1351
11.5	0.1461	0.1450	9.5	0.0374	0.0360	0.1447
16	0.1520	0.1511	14	0.0433	0.0436	0.1523
24	0.1572	0.1578	22	0.0485	0.0512	0.1599
32	0.1631	0.1620	30	0.0544	0.0544	0.1631

$$\log (0.18 - y) = (0.2553 - 1) - 0.315\sqrt[3]{t} \dots\dots \quad (16)$$

$$\log (0.057 - Y) = \log 0.057 - 0.045T \dots\dots \quad (17)$$

From the above tables it is evident that the results calculated by the usual velocity equation are in as good accord with the observed values, as are the results calculated by the empirical equation (3) proposed by the above authors.

Finally it should be observed that A, which is the maximum quantity of phosphoric anhydride which the liquid can extract, is not identical in Tables I and II, or in Tables III to VI. If the phenomenon being measured were one of solution only, this would of course, be a legitimate objection to these calculations. But it has been shown that when water acts on dicalcium phosphate or tricalcium phosphate a decomposition results, the solution having a higher ratio, $P_2O_5 : CaO$, than the remaining solid.[1] The same sort of hydrolysis undoubtedly takes place when carbonated water is used as a solvent. With a hydrolysis whose extent depends on the original ratio of salt to water, the quantity of phosphoric anhydride in solution at equilibrium depends on the quantity of salt originally employed, and hence A will vary with the conditions of the experiments.

---

[1] Cameron and Bell, *Bull.* 41, Bureau of Soils, U. S. Dept. Agr.

In this paper it has been shown that notwithstanding the conditions militating against the use of the ordinary equation for rate of solution, *viz.*: the variable extent of surface and the fact that the phenomenon observed is not one of solution only but also of hydrolysis, this equation describes the data at least as well as the empirical equation proposed by Mitscherlich, Kunze, Celichowski, and Merres.

The usual equation for rate of solution also describes very well the extraction of lime from a loam soil by carbonated water.

NOTES.

Red Lines for a Balance Scale.—Having occasion recently to purchase a balance, it occurred to me that, as color contrast is an aid to vision, it might be of assistance in reading the variations of the needle on a balance scale, and I therefore instructed the makers to equip the balance with an ivory scale having *red* lines, instead of the usual black ones.

This was done, and the result has justified my anticipations. The contrast between the black needle and the red lines on a white background is restful and pleasing to the eyes, and enables a close weighing with less eye-strain than with the black lines.

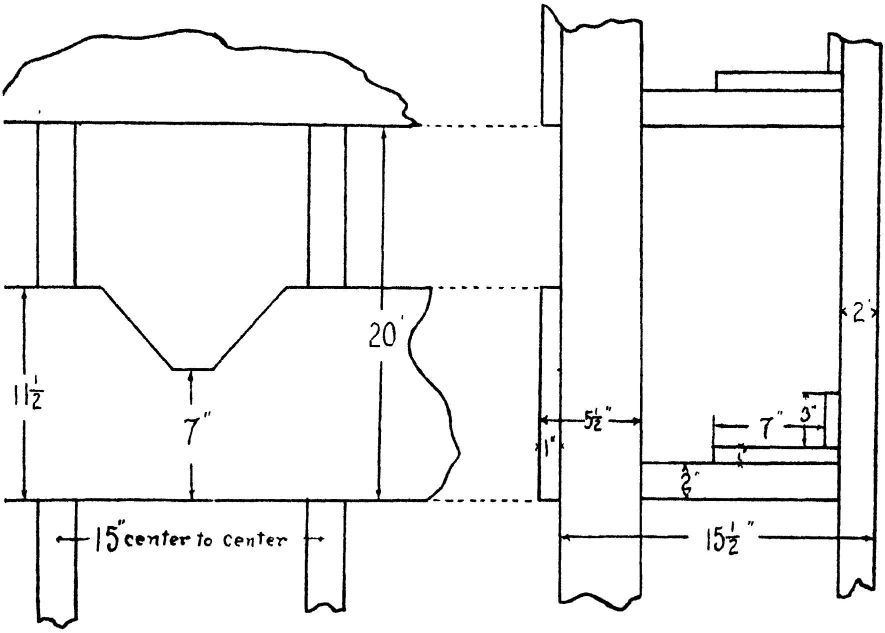
No extra expense was incurred in making the change from black lines to red, and I would recommend such innovation to those contemplating the purchase of a balance. C. M. CLARK.

Rack for Holding Reagents in Bulk.[1]—The bottle rack that we designed for our building to store the common stock solutions in five-gallon quantities is a framework of two-inch square material. Each row holds thirteen bottles, which are held apart, both in front and back, by uprights of the same material. For each bottle there is, therefore, a frame compartment. The bottles are kept from the wall by a three-inch board, nailed to the floor of each shelf at the rear of the rack. Along the front of each tier runs a board with a "V" shaped cut in the middle of each compartment on the sides of which the bottles rest. This prevents them from rolling. It also allows the bottles to be placed in the rack on their sides, at an angle which gives the maximum room for the solution and uses up the minimum amount of space. A glass siphon runs to the lowest portion of the bottle through a notched cork or rubber stopper, and is closed at the outer end by means of a rubber tube and a pinch clamp. Smaller bottles can thus be neatly and quickly filled without lifting the heavy, cumbersome stock bottles.

The solutions are made concentrated, according to a formula, and then the bottle is placed in the rack, and the siphon inserted. A rubber tube leading from the distilled water tap is then connected to the lower end of the siphon and the bottle filled. The strong current of water entering at the deepest part of the solution acts as sufficient stirrer to thoroughly mix the solution and secure uniform density.

---

[1] Published by permission of Dr. Charles Baskerville, Director of the Chemical Laboratory, College of the City of New York.



In this way a large number of bottles can be compactly stored and the solutions are easy of access. The framework structure allows the bottles to be cleaned without removing them from the rack, as they are exposed on all sides. All dirt can be brushed down into the inclined lead-lined drip trough at the base of the rack and flushed off. J. Lorenz Sporer.

[Contribution from the Bureau of Chemistry, U. S. Dept. of Agriculture.]

IS THE HYDROLYSIS OF CANE SUGAR BY ACIDS A UNIMOLECULAR REACTION WHEN OBSERVED WITH A POLARISCOPE?

By C. S. Hudson.

Received May 9, 1910.

It may be recalled that in 1908 Julius Meyer[1] expressed the view that the hydrolysis of cane sugar by acids is accompanied by two simultaneous reactions, the mutarotation of glucose and fructose, and published experiments which seemed to show that the hydrolysis when observed with the polariscope deviates slightly from the unimolecular order during the first 3 or 4 per cent. of the reaction. In the same year the author[1] showed that the hydrolysis of cane sugar by the enzyme invertase is certainly accompanied by these mutarotation reactions, but claimed that the acids catalyze the mutarotations so greatly that they are not of detectable influence in the hydrolysis of cane sugar by acids. Meyer's experiments, which seemed to show such an influence, were criticized on the ground that the possible errors in them were greater than Meyer had estimated and even greater than the deviation from the unimolecular order which he recorded. Essentially the same criticism has also been made by Bodenstein.[2] In a reply to these objections Meyer[3] has lately insisted on the great accuracy of his experiments and claims that he did indeed detect the mutarotation reactions during the hydrolysis of cane sugar by acids.[4] If the question were only a difference of opinion regarding the accuracy of Meyer's experiments the discussion could well be closed because all three parties are agreed on the principal point, namely, that the hydrolysis of cane sugar is not the simple reaction that it has heretofore been supposed to be, but is accompanied by two other important reactions. But Meyer goes further than this and claims[5] that he first proved experimentally the existence of these subsidiary reactions, and on account of this claim, which appears to me quite unwarranted, the following further criticism of Meyer's experiments is made. In it I will seek to show that Meyer has repeated portions of his measurements and found them to be entirely erroneous, that Armstrong and Caldwell made measurements similar to Meyer's four years in advance of him and found numbers which are different even in sign from Meyer's, that the deviation which Meyer claims he found is opposite in sign from that predicted by the very theory which he was testing, that certain obvious precautions which are necessary for the accuracy that Meyer attempted to reach were overlooked, and that his latest measurements contain certain self-evident errors of great size.

---

[1] *Z. physik. Chem.*, **62**, 59–88 (1908).

In Meyer's first article the mutarotation of fructose was found to have the velocity coefficients 0.017 at 18° and 0.027 at 25°. In response to a letter from me he has measured these values again and now finds 0.18 at 18° and 0.32 at 25°, values which are tenfold greater than his former ones. Although he thus admits that one set of his measurements was entirely incorrect, he insists that another set of a similar though not identical kind, namely that in which the minute deviation was supposedly detected, contains no error greater than about one-tenth of 1 per cent. The experiments were made under the same conditions, and great accuracy is claimed for one set and great error admitted for the other; comment would hardly seem necessary.

---

[1] This Journal, 30, 1160–6 (1908).

[2] *Z. Elektrochem.*, 15, 413 (1909).

[3] *Z. physik. Chem.*, 72, 117–23 (1910).

[4] In replying to my criticism Meyer has made an arithmetical error (p. 119) in which he confuses 3 per cent. with three-tenths of 1 per cent. and this difference refutes his own argument. It will be sufficient time to discuss the bearing of this portion of the reply after he publicly corrects this error. He has also confused α- and β-fructose on pp. 117 and 122.

[5] *Z. physik. Chem.*, 72, 117 (1910).

In 1904 Armstrong and Caldwell[1] made polariscopic measurements to test whether the hydrolysis of cane sugar by acids follows the unimolecular order and came to the conclusion that it does not, and that the velocity-coefficient of the reaction *increases* slightly during the inversion instead of remaining constant as is required by the theory. Meyer's measurements lead him to the conclusion that the velocity-coefficient *decreases* during the inversion. Meyer has not mentioned this work of Armstrong and Caldwell, nor the older work of O'Sullivan and Tompson,[2] who were the first to show that the mutarotation of glucose accompanies the inversion of cane sugar by invertase, nor the work of the author,[3] which shows that the mutarotation of both glucose and fructose follows slowly on the hydrolysis by invertase. It would seem that he should at least discuss the cause of the disagreement between his detection of the *decreasing* coefficient and Armstrong and Caldwell's of an *increasing* one, particularly in view of the fact, which I shall immediately explain, that a *decreasing* coefficient is not in agreement with the theory which Meyer was testing.

Meyer supposes that the mutarotation of glucose and fructose following the inversion of cane sugar would cause the reaction as measured by the polariscope to show a decreasing coefficient, and as he found a decreasing one in his experiments he claims that he has proved experimentally the correctness of the theory. The mutarotation of fructose proceeds so much faster than that of glucose that the influence of the former may be neglected in comparison with that of the latter. The glucose which is first formed is known to be α-glucose, of specific rotation 110°, and it subsequently passes to the stable mixture of α- and β-glucoses, of specific rotation 52°. If now the mutarotation of glucose is comparable in rate with the inversion of cane sugar, the glucose resulting from the hydrolysis will contain an excess of α-glucose and have a specific rotation higher than the stable mixture, 52°. As it is assumed in calculating the velocity-coefficient of the hydrolysis from the polariscopic readings that the glucose has the specific rotation 52°, the presence of an excess of α-glucose, due to the comparative slowness of the mutarotation reaction, must cause the inversion to appear slower than it really is. During the further progress of the inversion the excess of α-glucose diminishes and therefore the polariscopic readings in the late stages of the reaction give a true measure of the extent of the hydrolysis. Such a reaction, in which there is an error of this kind causing it to apparently go slower in its initial stages than it really does, must give an *increasing* velocity-coefficient during its progress. Meyer found however a *decreasing* coefficient, which is thus quite at variance from the theory which he claims he has proved by detecting such a coefficient. It would seem to the author that this point should be a conclusive objection to Meyer's claim that he proved the existence of the mutarotation reactions in the hydrolysis of cane sugar.

---

[1] *Proc. Roy. Soc. London*, 74, 195–201 (1904).

[2] *J. Chem. Soc.*, 57, 834–931 (1890).

[3] THIS JOURNAL, 30, 1160–6, 1564–83 (1908); 31, 655–64 (1909).

It is to be objected to the experiments of both Meyer and Armstrong and Caldwell that a source of considerable error was not considered, namely the fact that the specific rotation of fructose increases with its concentration; thus in the hydrolysis of a 20 per cent. cane sugar solution the fructose increases in concentration from zero to about 10 per cent., which involves according to the measurements of Hammerschmidt[1] and others, an increase of 2 per cent. in the specific rotation of fructose. If the progress of the inversion is calculated from the polariscopic readings under the assumption that the specific rotation of fructose remains constant during the reaction, the velocity coefficient must be expected to increase. The changing concentrations of glucose and cane sugar also involve similar corrections, but they are small in comparison with that for fructose. This error would affect the velocity coefficient in the same manner that the mutarotation of glucose would, and until it is accurately investigated it cannot be claimed that an *increasing* coefficient proves the occurrence of the mutarotation during the hydrolysis of cane sugar by acids; and of course the claim of Meyer, who found a *decreasing* coefficient, is quite unreasonable.

Lastly, as an illustration of the inaccuracies which occur in Meyer's measurements, and in refutation of his insistence that both Bodenstein and the author have done him the injustice of underestimating the accuracy of his work, it may be mentioned that he records[2] as the final rotations of two fructose solutions of the same concentration, prepared from the same sample, and measured in tubes of the same length, —14.40° at 25° and —14.41° at 18°. It is well known that fructose has one of the largest temperature coefficients of rotation ever found, namely 0.007° per degree of rotation per degree rise of temperature.[3] Other observers, including Dubrunfaut, Zecchini, Dafert, Hönig and Jesser, Jungfleisch and Grimbert, Wiley, Borntraeger, and Ost,[4] have invariably detected a change of rotation for such solutions of (14.40) (0.007) (7) = 0.69°, or over half a degree, but Meyer did not find any appreciable difference at the two temperatures. With this error of half a degree plainly visible in his published work it is impossible to agree with him that such readings as 40.45° and 40.41° differ beyond his experimental error; and yet the deviation from the unimolecular order which he found the inversion of cane sugar by acids to show, depends on the reality of the difference between such measurements.[1]

---

[1] *Z. Ver. d. Zuckerind.*, 41, 157.

[2] *Z. physik. Chem.*, 72, 122 (1910).

[3] Wiley, *Am. Chem. J.*, 18, 81.

[4] Lippmann's "Chemie der Zuckerarten," ed. 1904, Vol. I, pp. 823-5.

The rates of the inversion of cane sugar and the mutarotation of glucose at different temperatures and acid strengths have been measured by various investigators, and it is possible to calculate from them the deviation which is to be expected from the unimolecular order due to the mutarotation of the glucose. The author has made such a calculation and finds the deviation to be, under the most favorable conditions of temperature and acidity, a very small quantity only about a tenth of 1 per cent. It agrees in magnitude and sign with the deviation which Armstrong and Caldwell found and it is quite possible that the mutarotation reaction is responsible for a portion of their deviation, but the change in the specific rotation of fructose which has been mentioned, causes a deviation in the same direction and the two possible causes of the deviation leave the matter still in doubt as to whether Armstrong and Caldwell's deviation is due to mutarotation, change of rotation of fructose, or a true exception to the law of mass-action, which latter view is the one that Armstrong and Caldwell hold. But there can be no reasonable further doubt regarding the cause of Meyer's deviation—it was due to experimental errors alone, and is opposite in sign to the deviation predicted by theory.

A REVIEW OF DISCOVERIES ON THE MUTAROTATION OF THE SUGARS.[2]

By C. S. Hudson.

Received May 9, 1910.

Dubrunfaut[3] discovered in 1846 that the specific rotation of a freshly prepared cold solution of crystalline glucose decreases from an initial value of about 110° to become constant at 52°. This phenomenon he named *birotation* but later discoveries have shown the name to be inappropriate and the better term *mutarotation*, which was introduced by Lowry[4] in 1899, has generally replaced it, though the word *multirotation* is also in use. In addition to glucose the following crystalline sugars have been found to show mutarotation: lactose,[1] galactose,[2] arabinose,[3] maltose,[4] xylose,[5] fructose,[6] fucose,[7] rhamnose,[8] mannose,[9] rhodeose,[10] gentiobiose,[11] melibiose,[12] perseulose,[13] and several rare synthetic sugars. All of these sugars reduce Fehling's solution and combine with phenylhydrazine, proving that they are aldoses or ketoses and contain the carbonyl group; on the other hand such sugars as sucrose, raffinose, gentianose, and stachyose, and the polysaccharides starch, inulin, mannan, etc., and the glucosides salicin, amygdalin, helicin, arbutin, etc., none of which show the characteristic reactions for the carbonyl group, do not exhibit mutarotation. This proves that the mutarotation is in some way dependent upon the carbonyl group.

---

[1] See *Z. physik. Chem.*, 62, 59–88 (1908).

[2] Presented at the Second Decennial Celebration of Clark University, Worcester, Mass., Sept. 15, 1909.

[3] *Ann. chim. phys.*, 18, 99–107 (1846); 21, 178–80 (1847); *Compt. rend.*, 23, 38–44 (1846).

[4] *J. Chem. Soc.*, 75, 212–5 (1899).

After Dubrunfaut's great discovery the next important observation on mutarotation was made by E. O. Erdmann[14] in 1855, who noticed that lactose occurs in two crystalline modifications, one having a higher rotation (86°) than that of the stable solutions (52°), and the other a lower rotation (36°), and each form showing mutarotation towards the same final rotation (52°). Erdmann measured the rates at which each form changes in rotation to that of the stable solution, but did not notice that the rates are the same in value and that this fact is of much theoretical significance. Many years later, after the principles of chemical dynamics became better known, the author[15] showed that these equal rates prove that the two changes of rotation are not different reactions but are opposite parts of one balanced reaction. In this way the mutarotation of lactose, and what is true of this sugar is doubtless true of all which show mutarotation, was proved to belong to the great class of balanced reactions.[16]

In 1859 Anthon[17] noticed that crystalline glucose forms its saturated solutions in cold water very slowly even when the mixing is vigorous; this fact was discovered for lactose by Mills and Hogarth[18] in 1879. It is now known that this slowness of the process of solution is caused by the same slow balanced chemical reaction, involving the carbonyl group, which causes the mutarotation, and that it is a general property of all the aldehyde and ketone sugars.[1]

---

[1] E. O. Erdmann, *Fortschritte Physik.*, p. 13; *Fortschritte Chemie*, p. 671 (1855).

[2] Pasteur, *Compt. rend.*, 42, 347–51 (1856).

[3] Parcus and Tollens, *Ann.*, 257, 160–78 (1890).

[4] Soxhlet, *J. prakt. Chem.*, 21, 283 (1880).

[5] Koch, *Pharm. Ztg. Russland*, 25, 619, 635, 651, 667, 683, 699, 730, 747, 763 (1886).

[6] Jungfleisch and Grimbert, *Compt. rend.*, 107, 390–3 (1888).

[7] Guenther and Tollens, *Ber.*, 23, 2585–6 (1890).

[8] Parcus and Tollens, *Loc. cit.*

[9] Van Ekenstein, *Rec. trav. chim.*, 15, 221–4 (1896).

[10] *Z. Zuckerind. Böhmen*, 25, 297 (1902).

[11] Bourquelot and Hérissey, *Ann. chim. phys.*, 27, 397–432 (1902).

[12] *Z. Ver. d. Zuckerind.*, 53, 1050–9 (1903).

[13] Bertrand, *Compt. rend.*, 147, 201–3 (1908).

[14] *Loc. cit.* Also *Ber.*, 13, 2180–4 (1880).

[15] *Z. physik. Chem.*, 44, 487–94 (1903).

[16] Using the same method Meyer later proved this for glucose, *Z. physik. Chem.*, 62, 74 (1908). Cf. also Roux, *Ann. chim. phys.*, 30, 422–32 (1903).

[17] *Dingler's poly. J.*, 151, 213–23 (1859); 155, 386–8 (1860); 166, 69–71 (1862).

[18] *Proc. Roy. Soc. London*, 28, 273–9 (1879).

The first attempt to find the physical law which governs the rate of the mutarotation was made by Mills and Hogarth[2] in 1879, but the result was only an empirical formula and must be regarded as unsatisfactory. It is to Urech[3] that we owe the first real progress in this line. He showed by a series of experiments during 1882–5 that the mutarotation follows the law of unimolecular reactions. It is interesting, and to some minds instructive, to note that this correct beginning in the physico-chemical study of the long unsolved mutarotation reaction was coincident in time with the beginning of the modern theory of solutions and chemical dynamics. There can be little doubt that Urech's experiments, which are the starting point of all exact work on mutarotation, were suggested by the advances that were being made at that time in the study of chemical dynamics by the new physico-chemical school.

In 1888 Brown and Morris[4] and Arrhenius[5] observed that the freezing temperatures of glucose solutions remain unchanged during the process of mutarotation, which proves that the reaction which causes mutarotation is not a polymerization or dissociation of the sugar. More recently Roth[6] has detected a slight change in freezing temperature of concentrated solutions of anhydrous glucose on standing but this is doubtless due to hydration and does not alter the conclusion from the work of Brown and Morris and Arrhenius, because a polymerization or dissociation would also affect the freezing point of dilute solutions, and the investigators are all agreed that such an effect is not discernible.

In 1890 O'Sullivan and Tompson[7] noticed that the invert sugar which is produced by the hydrolytic action of the enzyme invertase on sucrose shows mutarotation; this fact was later investigated by E. F. Armstrong[8] and has been precisely studied lately by the author.[9] These researches have shown that the glucose which is liberated from sucrose is α-glucose and the fructose is a hitherto unknown form of this hexose, α-fructose; these facts show that sucrose has the constitution α-glucose $<>$ α-fructose. The new form of fructose has not as yet been obtained crystalline. This method for determining the constitution of the polysaccharides by studying the mutarotation of the sugars which are formed by their enzymotic hydrolysis was first used by E. F. Armstrong[2] in his correlation of the α- and β-methylglucosides with the α- and β-glucoses. In applying the method to other substances such as cane sugar where two mutarotating sugars are formed at the same time it is necessary to extend the theoretical considerations; a mathematical theory of the modified method of Armstrong and an experimental demonstration of it has recently been published by the author.[1]

---

[1] Hudson, *Z. physik. Chem.*, 44, 487–94 (1903); THIS JOURNAL, 26, 1065–82 (1904).

[2] *Loc. cit.*

[3] *Ber.*, 15, 2130–3 (1882); 16, 2270–1 (1883); 17, 1547–50 (1884); 18, 3047–60 (1885).

[4] *J. Chem. Soc.*, 53, 610–21 (1888).

[5] *Z. physik. Chem.*, 2, 491–505 (1888).

[6] *Ibid.*, 43, 539–64 (1903).

[7] *J. Chem. Soc.*, 57, 920 (1890).

[8] *Ibid.*, 83, 1305–13 (1903).

[9] THIS JOURNAL, 30, 1160–6, 1564–83 (1908); 31, 655–64 (1909).

In 1895 Charles Tanret[2] discovered a new form of crystalline glucose which was found to have a specific rotation lower than that of the stable solution (52°), though its value increased to this on standing. This discovery is the complement to Dubrunfaut's and the two must cause chemists the world over to be grateful to French science, because more fruitful single discoveries in the chemistry of the carbohydrates have hardly been made. Tanret found the final rotation of glucose solutions to be the same whether the solution is made from the higher or the lower initially rotating form. He interpreted his results as proving that three forms of glucose exist, one of high rotation, one of low, and the third the form to which each of these changes in aqueous solution. About the same time Tanret isolated similar new crystalline forms of rhamnose, galactose and arabinose, and obtained Erdmann's lower rotating form of lactose practically pure. Tanret's striking discoveries immediately caused new interest to be taken in the problem of mutarotation. In 1899 Lowry[1] advanced the view that the mutarotation of glucose is caused by a balanced reaction between the highest and lowest rotating forms of the sugar, a view which may be expressed by the equation *α-glucose* $\rightleftarrows$ *β-glucose*. This explanation is essentially different from any that preceded it and later investigations have proved it to be entirely correct. On the other hand, Lowry did not support this hypothesis with any direct proof and it remained without such proof for several years. In 1902[3] the author published the same view as an explanation of the mutarotation of lactose, being at that time unacquainted with the publication of Lowry. The explanation may be expressed by the equation α-lactose $\rightleftarrows$ β-lactose, and experimental evidence for the view was given by measurements on the heats of solution of the three forms of lactose, which showed that the stable form to which α- and β-lactose change in solution is not a chemical individual, as Tanret had supposed, but is a mechanical mixture of α- and β-lactoses. In 1903 the author[4] measured the slow maximum rate of solution of α-lactose and showed that the slowness of dissolving, which had been discovered by Mills and Hogarth,[1] is caused by the balanced reaction which produces the mutarotation. By quantitative measurements the hypothesis of the balanced reaction was tested and proved, and the explanation which these measurements gave of the mutarotation of lactose was immediately accepted by such an authority as Nernst.[5] In the same year Lowry[6] published similar experiments on glucose and proved the suggestion which he had advanced in 1899. These questions of priority are here stated for the reason that E. F. Armstrong[7] has recently claimed for Lowry the discovery of the balanced reaction which causes the mutarotation, a claim which in the opinion of the author is entirely too broad.

---

[1] *Loc. cit.*

[2] *Bull. soc. chim.*, 15, 195–205, 349–61; 17, 802–5.

[3] Princeton Univ. *Bull.*, April, 1902.

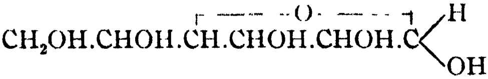
[4] *Z. physik. Chem.*, 44, 487–94 (1903).

[5] "Theoretische Chemie," ed. 1904.

[6] *Proc. Chem. Soc.*, 19, 156–7 (1903); 20, 108–9 (1904).

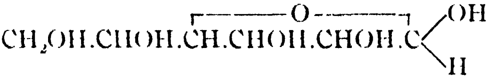
[7] "The Simple Carbohydrates and Glucosides," p. 8.

A very fruitful idea was advanced by Lippmann[1] in 1895 in the suggestion that the lactonic formula for glucose predicts two possible forms of the sugar on account of the asymmetry of the end carbon atom, the two structures being



$$CH_2OH.CHOH.\overbrace{CH.CHOH.CHOH.C}^{O}\begin{smallmatrix}H\\OH\end{smallmatrix}$$

and



$$CH_2OH.CHOH.\overbrace{CH.CHOH.CHOH.C}^{O}\begin{smallmatrix}OH\\H\end{smallmatrix}.$$

This suggestion, after a slight development by Simon,[2] was made more probable by Armstrong's discovery,[3] that the α- and β-forms of methyl glucoside are hydrolyzed by enzymes to give methyl alcohol and the α- and β-forms of glucose respectively. As the methyl glucosides show no aldehyde reactions the lactonic formulas have always been chosen for them, the hydroxyl of the end carbon atom in the structures shown above being replaced by the group OCH_3. Armstrong's discovery indicates that similar structures probably apply to the forms of glucose. This suggestion received final proof in 1909 when the author[4] showed that certain numerical relations which can only be explained by the assumption of such lactonic structures for the two forms of the sugar, hold all through the sugar group. If the rotation of the end carbon atom is B for one structure it must be $-B$ for the other, and if A is the rotation of the remaining asymmetric carbon atoms, which are common to both structures, the total rotation of the one structure is $A + B$, and of the other structure $A - B$, the difference between the two total rotations being then $2B$. This rotation B applies to all the aldoses because they contain the same end asymmetric carbon, therefore the difference between the molecular rotations of the α- and β-forms of all the aldose sugars should be a constant quantity if the sugars have the two isomeric lactonic structures. The molecular rotatory powers of the two forms of lactose, glucose, arabinose and galactose were found indeed to differ by the quantities 17600, 16000, 16200, and 15700, which are sufficiently alike to show that the theory is correct and that the two forms of each of the mutarotating sugars have the stereomeric lactonic structures. Certain other similar conclusions from the same theory were also found to agree with the rotatory powers of the sugars and their glucosidic derivatives.

The catalytic action of various substances on the mutarotation reaction has been investigated by various chemists.[5] These researches have shown that only acids and alkalies have a strong action. Osaka[6] made the first quantitative study of the relation between acidity or alkalinity and catalytic action and found that the catalysis is proportional to the concentration of the hydroxyl ions and proportional to the square root of that of the hydrogen ions. Later the author[1] showed that the proportionalities are somewhat different from this and that the rate of the mutarotation of glucose is related to the acidity and alkalinity of the solution by the expression *rate* = $A + B(H^{\cdot}) + C(OH')$, where A, B, and C are constants at constant temperature. This formula has lately been used as the basis of a new method for measuring the electrolytic dissociation of water.[2] A satisfactory explanation of the fact that acids and alkalies are enormously powerful catalysts of the mutarotation while all other substances are without comparable action is lacking.

---

[1] "Die Chemie der Zuckerarten," ed. 1895, pp. 130, 990, 992.

[2] *Compt. rend.*, 132, 487–90 (1901).

[3] *Loc. cit.*

[4] This Journal, 31, 66–86 (1909).

[5] Levy, *Z. physik. Chem.*, 17, 301–24 (1895); Trey, *Ibid.*, 18, 193–218 (1895); 22, 424–63 (1897); 46, 620–719 (1903); Simon and Bénard, *Compt. rend.*, 132, 564–6 (1901); Lowry, *J. Chem. Soc.*, 83, 1314–23 (1903).

[6] *Z. physik. Chem.*, 35, 661–706 (1898).

The sugars glucose, lactose, galactose, rhamnose, melibiose, arabinose, maltose, xylose and some others occur as monohydrates and these have generally been regarded as hydrated aldehydes without lactonic structure and thus intermediate forms between the two lactonic α- and β-forms of the sugars. The freshly prepared solutions of these monohydrates are identical in properties with such solutions of one of the anhydrous lactonic forms of the sugars and it is therefore to be concluded that the equilibrium between this lactonic form, whichever it may be, and the monohydrate is established instantly. For most of the sugars the lactonic form which is thus in instantaneous equilibrium with the monohydrate is the α-form, but for one sugar at least, maltose, it is the β-form. The mutarotation reaction may then be considered to be the slow change of the monohydrate into the other lactonic form by a reversible reaction, or in the form of an equation,

$$\alpha\text{-sugar} + H_2O \underset{(1)}{\rightleftharpoons} \text{monohydrate} \underset{(2)}{\rightleftharpoons} \beta\text{-sugar} + H_2O.$$

For most of the sugars the reaction 1 is instantaneous in comparison with 2, which is therefore the mutarotation reaction, but for maltose the relations are reversed. Why the monohydrate should change instantly to the α-form for some sugars, but to the β-form for others is entirely unknown and is a most interesting problem.

The mutarotation reaction is general to all the aldehyde and ketone sugars. It may indeed be called the fundamental reaction of the sugar group. While its cause remained unknown during the half century following its discovery, the last decade has brought a full explanation of it. The principal facts regarding it have been accurately measured and correlated. On the other hand the application of these facts to the elucidation of the chemical and biological reactions of the sugars, in every one of which mutarotation plays a part, has just begun, but it is even now apparent that the unfolding chemistry of the polysaccharides is to be largely a development of the mutarotation reaction.

BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

RECENT PUBLICATIONS.

AUFHÄUSER: **Vorlesungen über Brennstoffkunde. Hamburg: Boysen & Maasch. 8°, 2 M.**

BAUD, E.: **Industries des acides minéraux. Acides sulfurique chlorhydrique et azotique. Paris: 8°, 380 pp., 4 M.**

---

[1] THIS JOURNAL, 29, 1571-6 (1907).

[2] *Ibid.*, 31, 1136-8 (1909).

BATTEGAY, A.: **Conférences de pharmacie, Tome 4. Analyses d'urines, de fèces, de lait.** 8°, 48 s., 2 Fr.

BOLTZMANN, L.: **Vorlesung über Gastheorie. (2 Teile) Teil I: Theorie der Gase mit einatomigen Molekülen, deren Dimensionen gegen der mittlere Weglänge verschwinden. 2, unveränderter Abdruck.** Leipzig: 8°, 6 M., Teil II, 7 M.

BÜCHER: **Der Naturwissenschaft.** Herausgegeben von S. GÜNTHER. 4 Band. G. BUGGE, **Strahlungserscheinungen, Ionen, Elektronen und Radioaktivät.** Leipzig: 138 s., 0.80 M.

DESALME J. ET PIERRON, L.: **Couleurs, peintures et vernis.** 18, 456 s., 5 Fr.

ENNIS, W. D.: **Linseed Oil and Other Seed Oils.** London: 8°, 350 pp., cloth, 16.50 M.

ESCARD, J.: **Les matières abrasives industrielles.** 8°, 170 s., 10 Fr. **Les métaux spéciaux manganèse, chrome, silicium, tungstène, molybdène, vanadium, et leurs composés métallurgiques industriels.** 8°, 594 s., 19.50 Fr.

FOLTZER, J.: **La soie artificielle et sa fabrication.** 2 edition, refondue. Paris: 144 pp., 12.50 M.

FRANKE, H.: **Die pflanzlichen Gerbstoffe. Uebersicht über Vorkommen, Eigenschaften, Gewinnung und Anwendung der wichtigeren pflanzlichen Gerbstoffe.** Magdeburg, kls., 67 pp., 3 M.

FRITSCH, J.: **Fabrication du chocolat.** 8°, 350 pp., 25 Fr.

Handbuch der Biochemischen Arbeitsmethoden. Herausgegeben von E. ABDERHALDEN (3 Bände) Wien, Band I jetzt vollständig. 27 M.

HILLEBRAND, W. F.: **Analyse der Silicat und Carbonatgesteine.** Deutsch von E. WILKE-DÖRFURT. Zweite vermehrte Auflage der Praktische Anleitung zur Analyse der Silicatgesteine. Leipzig: Wilh. Engelmann. 8°, 258 s., 8 M.

HOFFMANN, M. K.: **Lexikon der Anorganischen Verbindungen.** Dictionary of Inorganic Compounds. Dictionaire des Combinaisons Minérales. Dizionario delle Combinazioni Inorganiche. Leipzig: 8°, Jede Lieferung, 4 M

HOLLEMAN, F. A.: **Trattato di chimica inorganica,** 3 ed., Mailand, Societè Edit. Libiraria. 8°, 497 s., 13 L.

JONES, H. C.: **Introduction to Physical Chemistry.** London: 8°, cloth, 7.50 M.

NIEWENGLOWSKI, G. H.: **Traité pratique de photographie des couleurs.** 18, 4 Fr.

OSTWALD-LUTHER: **Hand- und Hilfsbuch zur Ausführung physico-chemischer Messungen.** Dritte Auflage. Herausgegeben von Prof. Dr. R. Luther. Leipzig: W. Engelmann. 8°, 573 s., 13 M.

OSTWALD, W.: **L'évolution de la chimie.** 18, 364 s., 3.50 Fr.

OTTO MYER: **Handbuch der Kaliwerke, Salinen, Tiefbohrunternehmungen und Petroleum Industrie.** Leipzig: 12 M.

OUVRARD, L.: **Industrie du chrome, du manganèse, du nickel et du cobalt.** Paris: 8°, 320 pp., 4.50 M.

PASSON, DR. MAX: **Kleines Handwörterbuch der Agrikulturchemie.** Leipzig: W. Engelmann. 2 Bände.

POZZI-ESCOT, E.: **Les synthèses dans le groupe de l'indigo.** 18°, 108 s., 1.50 Fr.

PUBLOW, C. A., AND TROY, H. C.: **Questions and Answers on Milk Testing.** 8°, K. Paul, 2 s., 6 d.

RAGNO, S.: **La soudure autogène des metaux.** 8°, 90 s., 2.50 Fr.

RENGADE, E.: **Analyse thermique et métallographie microscopique.** 8°, 176 s., 6 Fr.

RINNE, F.: **Zur chemisch-mineralogischen Erforschung der Deutschen Kalisalzlagerstätten.** Leipzig: 8°, 32 s., 0.8 M.

RÖTTGER, PROF. H.: **Lehrbuch der Nahrungsmittel-chemie.** IV vermehrte und verbesserte Auflage. Leipzig: J. A. Barth. 1 Band, 601 s., 11 M.

RUSKA, J.: **Leitfaden der Mineralogie.** Einführung in das Verständnis der Erscheinungen und Kenntnis der Gebilde des Mineralreiches. Leipzig: 8°, 152 s., 2 M.

SÉRAND: **Le pain, fabrication rationelle historique.** 8°, 162 s., 4.50 Fr.

SONCINI, T.: **L'ambiente chimico ed i fermenti selezionati.** Lodi. 8°, 36 pp., 2.50 M.

SOMMERFELD, P.: **Milch und Molkereiprodukte; ihre Eigenschaften, Zusammensetzung und Gewinnung.** Leipzig: 8°, 140 s., 1 M.

STIFT, A., UND GREDINGER, W.: **Der Zuckerrübenbau und die Fabrikation des Rübenzuckers, nach den neuesten Erfahrungen der Wissenschaft und der Praxis.** Wien: Gr. 8°, Gebunden., 22 M.

THALMANN, F.: **Die Fette und Oele, Darstellung der Gewinnung und der Eigenschaften aller Fette, Oele u. Wachsarten, der Fett u. Oelraffinerie u. der Kerzenfabrikation.** 3, vermehrte Auflage. Wien: 8°, 3 M.

UNDERBERG, G.: **Le diamidophenol acide en photographie.** 8°, 32 pp., 6 Fr.

WEBER, C. O.: **The Chemistry of India Rubber.** 3rd. impress. London: C. Griffin. 8°, 326 pp., 16 s.

WICKENDEN, W. E.: **Illumination and Photometry.** Hill Pub. Co. 8°, 8 s., 6 d.

VOL. XXXII. AUGUST, 1910. No. 8.

THE JOURNAL

OF THE

American Chemical Society

[COMMUNICATION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

STUDIES IN VAPOR PRESSURE: I. A METHOD FOR DETERMINING UNDER CONSTANT CONDITIONS THE BOILING POINTS OF EVEN MINUTE QUANTITIES OF LIQUIDS AND OF NON-FUSING SOLIDS.[1]

BY ALEXANDER SMITH AND ALAN W. C. MENZIES

Received June 11, 1910.

For solids which do not melt, no method of determining the boiling point ("vaporizing point") that is at once simple and accurate is available. The chemist, when he encounters such a material, is thus deprived of both of his favorite methods for the characterization of substances. The crude plan of heating the substance in a deep crucible, placed in a draft cupboard, and taking the temperature of the vaporizing solid[2] is highly inconvenient, is very wasteful of material and, as we shall see, is not accurate.

The measurement of the boiling point of a liquid, as usually made by means of a distilling flask and thermometer, is open to several objections. One of these is that, even if the whole of the mercury thread of the thermometer is immersed in the vapor, the apparatus is not such that the other conditions can be exactly specified and constantly fulfilled. Varying results are therefore obtainable with the same substance by different observers, or even by the same observer. Thus, it is a familiar fact that use of a larger flame will raise the apparent boiling point. Again, use of a sand bath, a metal bath, or a wire gauze may cause superheating of the thermometer by radiation.

---

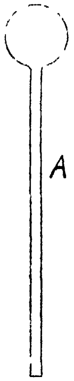
[1] Read before the American Chemical Society, Dec. 30, 1909.

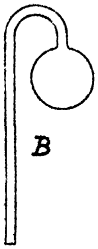
[2] V. Meyer and Harris, *Ber.*, 27, 1482.

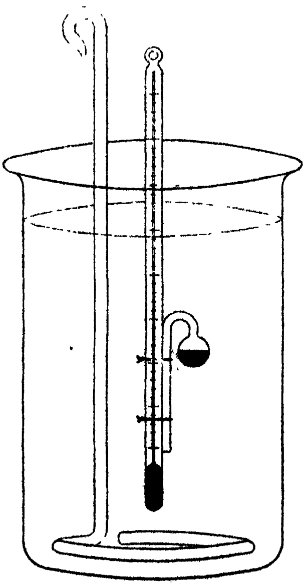
On the other hand, many liquids are easily superheated, and boil irregularly in consequence.

When the liquid boils regularly, use of a small flame, playing on the naked bulb of the flask and touching the latter only below the level of the surface of the liquid, gives the most constant and easily reproducible results. But trial will show that at least five minutes' continuous boiling is required before the thermometer reaches the true temperature. Unless the liquid is distilling over very slowly during this time, a considerable supply of the material is thus required, and must be prepared. Even if the boiling point were to be determined in a vessel attached to a reflux condenser, at least 10–20 cc. of the liquid would be required to wet the condenser and leave a sufficient amount of the liquid to cover the flame.

Surrounding the bulb of the thermometer with cotton[1] may protect the instrument from contact with superheated vapor arising from a "bumping" liquid, and so overcome one of these objections. But cotton is a bad conductor, and the air it contains is very slowly expelled, so that its use will be found to triple the time elapsing before the thermometer reading reaches the true boiling point. Its employment involves the provision of a slightly larger supply of the substance than would ordinarily be required.







Use of the apparatus here described enables one to avoid all these objections. The method automatically provides that constancy of conditions required for securing unvarying results. It enables one, also, to determine the boiling point of a solid as easily as that of a liquid. The whole operation takes no more time, and but little more of the substance than the measurement of a melting point, made with a like degree of accuracy.

The Apparatus.—A small bulb, with a wide capillary tube 3–4 cm. long and not less than 1 mm. in width

---

[1] Sydney Young, Stoichiometry (London, 1908), 141.

(figure, A) is prepared as for organic combustion of a liquid. The capillary is bent close to the bulb (figure, B), and a small amount (0.03-0.1 g.) of the liquid, or of the pulverized solid, is introduced (the latter most easily before bending). To exclude moisture, liquids may be distilled directly into a crucible or small test tube placed in a Brühl receiver, suitably desiccated. The bulblet stands stem downwards in, or hangs on the edge of, thec rucible. When the receiver is partially exhausted, and air is again admitted, the liquid enters the bulb. The bulblet, after being charged, is attached with thread or asbestos cord above the bulb of the thermometer. Use of wire is apt to cause breakage of the latter. The whole is then fixed in a beaker (preferably of tall form) filled with a transparent liquid, and provided with a glass stirrer, all just as for a melting-point determination (figure).

The Bath Liquid.—For substances boiling below 100°, the beaker may usually be filled with water, or a strong solution of calcium chloride. For substances boiling below 200°, sulphuric acid, and for those boiling as high as 280–300° melted paraffin wax (m. p. about 53°) may be employed. With substances boiling between 220° and 450° (or higher) we have used a eutectic mixture of potassium and sodium nitrates.[1] To extend the range downwards (to 120°), lithium nitrate may be added, but above 250° the lithium nitrate damages the thermometer and beaker by slowly attacking the glass and rendering it opaque. The composition of the mixtures is as follows:

$NaNO_3$.	KNO_3.	$LiNO_3$.	M. p.
18.18	54.54	27.27	120°
45.5	54.5	...	218°

When the nitrate baths are used, the melt is poured into an iron or porcelain dish and not allowed to solidify in the glass beaker. To secure a transparent liquid from a formerly turbid one, the outside of the solidified mass may be washed before being again used. The whole apparatus stands over a metal tray (*e. g.*, a "drip-pan"), which, in case of accidental breakage, catches the molten salts.

The Manipulation.—The apparatus being in order, the bath is heated and, as the boiling point is approached, is stirred vigorously. At first, a few bubbles of air are expelled in consequence of expansion. When the boiling point is reached, all the air in the submerged bulblet is quickly displaced and, provided the substance is not soluble in the bath liquid, bubbles of the vapor of the substance rise to the surface in a rapid and regular stream. On removing the flame, a fall in temperature by a small fraction of a degree interrupts the stream sharply, and a re-elevation by the same amount restores it. Since all solids have air and moisture adhering to their surfaces, and liquids are likely to contain oxygen and nitrogen and traces of water dissolved in them, a gentle stream of bubbles is allowed to pass off for a few moments before the temperature is allowed to fall preliminary to the final temperature reading. This reading is taken when, with very slowly falling temperature, accompanied by vigorous stirring, the stream of bubbles ceases. This applies only to the case of mutual insolubility of the substance and bath liquid: the procedure in the contrary case will be described presently.

---

[1] Carveth, *J. Physic. Chem.*, 2, 207; see also Scudder, This Journal, 25, 161.

The whole process should be repeated until constant readings are secured. To prevent the entrance into the bulb of the liquid from the bath, the thermometer and bulblet are finally raised out of the liquid. The barometric height (reduced to mercury at 0°) is recorded, as usual, along with the observed temperature. A necessary correction will be discussed later.

If the substance is soluble in the bath liquid, the temperature at which vapor ceases to issue cannot be observed sharply. The temperature reading is therefore taken when the bath liquid has ascended the capillary to a predetermined point, 5–10 mm. from the opening. The position of this point may be fixed by noting some mark on the thermometer or binding threads. When the substance is very soluble in the bath liquid, as alcohol is in water, the bubbles of vapor dissolve, instead of rising to the surface, and only the few bubbles of air are seen. When, in such a case, the flame is removed, and the bath liquid enters the capillary, the section of the latter is so small that the surface layer of the liquid within it quickly becomes saturated with the vapor of the substance. Hence the vapor cannot any longer dissolve nearly as fast as fresh vapor can be evolved from the substance in the bulblet. The level reached in the capillary is therefore unaffected by the tendency to absorb the vapor, and is fixed solely by the vapor pressure of the substance, which is slowly diminishing as the temperature falls.

The fact that the bath liquid may have considerable vapor pressure of its own—as, for example, when the boiling point of benzene is being determined with water as the bath liquid—has no influence on the observed boiling point. Such an influence would be observed only if the vapor of the water were able to diffuse up the capillary so as to reach the surface of the substance contained in the bulblet, and this it has no opportunity to do when the methods are used as directed. In particular the second method, involving ascent of the bath liquid into the capillary, should not be used with insoluble vapors. When thus no process of solution is occurring, the vapor of the substance is stationary and very slowly condensing. A little of the vapor of the bath liquid, if the latter has any appreciable vapor pressure, may then diffuse backwards into the bulblet. When, in such circumstances, the reading is made too deliberately, the dilution of the vapor in the bulb may lead to the reading of a temperature 0.05–0.1° too low.

Even when the vapor of the substance interacts chemically with the material in the bath, the boiling point will usually be still determinable. Thus, we have obtained serviceable boiling points of calomel with a bath of melted nitrates, although the vapor causes a slow precipitation of mercuric oxide; and of ammonium chloride, although the vapor interacts with the nitrates, giving rise to a continuous formation of nitrous oxide. In the latter instance, the temperature at the point of minimum gas-evolution was taken.

Correction for Immersed Depth.—Since the pressure, due to the height of the liquid in the beaker over the opening of the capillary in the first method, or over the point to which the liquid ascends in the capillary in the second, will raise the boiling point above that shown in an open flask, a correction of the barometric reading for this effect is required. The depth from the surface to the end of the capillary, or to the mark opposite the point to which the liquid ascended, is measured by means of a scale held in front of the beaker. This distance (in mm.) is multiplied by the specific gravity of the liquid at the temperature used and divided by the specific gravity of mercury at 0° (13.59). The result is added to the barometric reading. For ordinary purposes this distance and the specific gravity of the liquid do not need to be known with great accuracy. An error even remotely approaching 0.2 mm. of mercury in the pressure, representing an error of 2.7 mm. in the measurement of immersed depth when water is the bath liquid, could not possibly be

Sulphuric acid (92.75%)		Paraffin (M. p. 53°).		Two nitrates (Na and K).		Three nitrates (Na, K and Li).	
30°	1 818	60°	0.778	230°	1.968	120°	2.002
40	1.809	70	0.772	240	1.961	130	1.993
50	1.799	80	0.767	250	1 954	140	1.985
60	1.790	90	0.761	260	1.947	150	1.977
70	1.781	100	0 755	270	1.940	160	1.969
80	1.771	110	0.749	280	1.933	170	1.962
90	1.762	120	0.743	290	1.926	180	1.954
100	1.753	130	0.737	300	1.918	190	1.946
110	1.744	140	0.730	310	1.911	200	1.939
120	1.735	150	0.724	320	1.903	210	1.931
130	1.726	160	0.718	330	1.896	220	1.924
140	1.717	170	0.712	340	1.888	230	1.917
150	1.708	180	0.706	350	1.880	240	1.910
160	1.699	190	0.699	360	1.872	250	1.903
170	1.690	200	0.693	370	1.865	260	1.896
180	1.682	210	0.687	380	1.857	270	1.890
190	1.673	220	0.680	390	1.848	280	1.883
200	1.664	230	0.674	400	...	290	1.877
..	...	..	...	..	...	300	1.870

made. Yet such an inconceivable error would usually involve a difference of only 0.01° in the boiling point.

The above table of specific gravities[1] may be used in making the correction. For intermediate temperatures, the value is obtained by linear interpolation.

Precautions for Special Accuracy: *Stirring, Thermometry, Capillarity.*—(1) It is necessary that temperature changes near the boiling point should proceed very slowly, and that uniform distribution of temperature be secured by violent stirring.

(2) The thermometer must be accurate, or its errors known. The usual correction for exposed thread must be made. Use of short thermometers, with a range of only 50–60° each, and of a deep beaker, will permit complete immersion of the whole thread and render this correction unnecessary. The accuracy of the readings is ordinarily limited only by the accuracy of the thermometers used.

(3) Since the tendency to capillary rise in the narrow tube contributes an added pressure, and slightly elevates the boiling point, a capillary less than 1 mm. in diameter should not be employed.

It might be expected that this pressure, due to capillary ascension, would involve an appreciable error, but this is not the case. It is true that water has an exceptionally high capillary constant—at 0° nearly 31 mm. for a tube 1 mm. in diameter, and at 100° about 25 mm. In the single case, therefore, in which the substance and the bath liquid are both pure water, this pressure amounts to 1.7 mm. of mercury, and raises the boiling point 0.06°. But the capillary constants of other liquids are usually much smaller. Thus, the ascents in a tube 1 mm. in diameter are: paraffin oil (at 100°) 10.8 mm. (= 0.6 mm. Hg), sulphuric acid (at 100° 9.8 mm. (= 1.3 mm Hg). With the nitrates, however, *when pure*, the ascent is very high. Thus the ascent of the two nitrates in a tube 1 mm. in diameter is 23.4 mm. at 270° (= 3.3 mm. Hg). When water is the bath liquid, and some other substance is contained in the bulb, then the capillary ascension of the water contaminated with the distillate is not that of water alone, but very nearly that of the substance. Thus, when the substance is one miscible with water, such as alcohol, the capillary ascent, assuming 50 per cent. alcohol within the capillary, is 10.4 mm. (= 0.7 mm. Hg). When the substance is one immiscible with water, the ascent, as is well known, is greatly reduced by the oily matter in the liquid and the tube. In the case of benzene and water, for example, at 0°, it is only about 14 mm. (= 0.9 mm. of Hg). The ascent of the nitrates is likewise reduced. Thus, when the tube is wet with an organic substance which does not mix with the salts, the elevation is of the order of the smallest of the foregoing values. Thus the correction, if any be made on this account, represents only about 1 mm. of mercury, which would raise the boiling point on an average about 0.04°. The temperature readings must therefore be accurate to less than 0 04° to justify the use of this correction. When correction on this account is desired, the capillary rise may be measured to the nearest mm. by severing the bulb from the capillary tube, wetting the interior of the latter with the substance, and dipping the tube in the bath liquid.

---

[1] These specific gravities were determined in this laboratory by Mr. F. B. Plummer, to whom we desire to express our indebtedness. The values are accurate to within one unit in the third place of decimals. The following formulas summarize the results, and give values correct to the second decimal place within the limits of temperature specified:

Sulphuric acid (92.75%, 30–200°), 1.818–0.000906 (t — 30).
Paraffin (m. p. 53°, 60–230°), 0.778–0.000612 (t — 60).
Two nitrates (230–390°), 1.968–0.00075 (t — 230).

Examples.—The following sample boiling points (not corrected for capillarity) show: (1) that the correspondence of the results given by the submerged bulblet method (column 6) with those given by the distilling flask method[1] (col. 7), both obtained with the same thermometer, is satisfactory; (2) that this correspondence is as good whether the substance is very soluble or is insoluble in the bath liquid (col. 2); (3) that the correspondence is equally good whether the bath liquid has itself a high or a low vapor pressure at the temperature concerned; (4) that the correspondence in the case of solids is also satisfactory so far as data for comparison are obtainable:

Substance.	Bath liq.	Immersed depth.	Density of bath liq.	V. p. increase for 1°.	B. p. subm bulblet.	B. p. dist. flask.
Benzene	Water	113	0.97	24	79.01°	79.00°
"	H_2SO_4	104	1.77	..	79.04	79.00
"	Min. oil	60	0.9	..	79.35[2]	79.33[2]
Ether	$CaCl_2$ sol.	70	1.47	27	33.87	33.85
"	Water	73	0.99	..	33.91	33.85
Alcohol	Water	60	0.97	31	77.56	77.55
Camphor	Paraffin	45	0 69	20	208.00	207.65
Naphthalene	3 Nitrates	68	1.93	17	217.68	217.73
Calomel	2 Nitrates	59	1.85	..	383.2	[382.5]
Com. am. carbonate	Olive oil	57	0.88	..	58.5	[58.5]

For the sake of comparison, the results for liquids by the submerged bulblet (col. 6), being obtained under greater pressure than those in the open flask (col. 7), are reduced to the existing atmospheric pressure by means of the known vapor pressure changes for 1° (col. 5).

The value for calomel in col. 7 is taken from vapor pressure measurements made by ourselves, using a platinum resistance thermometer.

---

[1] Naked flask, flame below the level of the liquid, and boiling continued to constant reading.

[2] These observations were made at a different barometric pressure from the preceding ones.

Since a mercury thermometer, even when nitrogen-filled under pressure, and calibrated by comparison with a resistance thermometer, is accurate only ±1° at temperatures above 300°, this correspondence is satisfactory. V. Meyer (*loc. cit.*), using an open crucible, found the temperature of the vapor 357° (corr.), the error by his method being therefore 25.5°.

The vaporizing temperature of commercial ammonium carbonate is necessarily variable, since the substance is not of constant composition. The value in col. 7 is the mean of two values (59.6° and 57.6°, respectively) taken from Naumann's[1] and Isambert's[2] measurements of the vapor pressures of ammonium carbamate, and is therefore not strictly comparable.

Probably because the liquid is heated equally from all sides, and not merely from below, no tendency to "bumping" was observed.

Impure and Decomposing Liquids.—The submerged bulblet method will not only give the boiling point of a pure liquid, but has, in addition, the advantage of showing promptly when a mixture, and not a pure liquid, is being handled. If a second reading, following a second brief period of boiling for the removal of the volatile substances possibly present, shows a divergence from the first reading, the boiling or distilling operation can be repeated again and again. Since at most only two drops of material have been taken, as much as half of the sample can be boiled away in two or three minutes, and another observation made. If a continuously changing series of boiling points is observed, then the substance is impure (either originally, or in consequence of rapid decomposition). These operations are essentially fractionations, involving, however, only minute amounts of material and an insignificant expenditure of time.

To illustrate the behavior of a mixture, equal volumes of benzene and commercial toluene were taken, and 0.03 cc. of this mixture was used. The successive boiling points, with sulphuric acid as bath liquid, were 91.1°, 92.7°, 94.0°, 96.1°, 98.7°. After five observations, about half the contents of the bulblet still remained.

Characteristics of the Submerged Bulblet Method.—The chief features of the method are:

(1) That it is applicable to non-fusing solids, for the determination of the boiling points of which no simple and accurate method has been known.

(2) That a minimum of material[3] (at most 0.1 g.), and a minimum of time are consumed.

---

[1] *Ber.*, 4, 782.

[2] *Compt. rend.*, 97, 1212.

[3] For other methods requiring but little material cf. Sivolobov, *Ber.*, 19, 765; Mulliken, "Identification of Pure Organic Compounds," Vol. I, p. 282 (1904); Schleiermacher, *Ber.*, 24, 944.

(3) That the conditions are definite and easily reproducible with exactness, and that, in particular, it is impossible for the liquid, the vapor, and the thermometer to differ in temperature. The boiling points ascertained are therefore more accurate, and more exactly comparable than are those obtained by the usual method.

(4) That with impure or decomposing liquids a fractional distillation in miniature may quickly be carried out and the impureness recognized.

(5) That when the dissolved or occluded gases, or volatile substances which are always present, can be removed by boiling, the removal may be accomplished and a satisfactory boiling point secured.

(6) That by taking the boiling point of a mixture of the two, the identity or non-identity of two liquids of almost identical boiling points may often be ascertained without sacrifice of an appreciable amount of material. This method will apply, however, only when the two substances are of chemically dissimilar natures, and not usually to very similar substances.[1]

(7) That the method may be adapted to finding boiling points at normal pressure (760 mm.), and under reduced pressure (see next two papers).

[COMMUNICATION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

A COMMON THERMOMETRIC ERROR IN THE DETERMINATION OF BOILING POINTS UNDER REDUCED PRESSURE.

BY ALEXANDER SMITH AND ALAN W. C. MENZIES.

Received June 11, 1910.

In very accurate work, when the thermometer is immersed in a bath of liquid, a correction is introduced on account of the apparent elevation of the temperature, due to compression of the bulb. The converse effect, namely, a dilatation of the bulb, causing an apparent lowering in the temperature, when the thermometer bulb is immersed in a vapor under reduced pressure, may be equally well known. Having had occasion, however, to study a large part of the literature of boiling points and vapor pressures, we have not happened to observe any mention of this source of error, or any case in which a correction was applied on account of it.[2] This source of error would appear therefore to be neglected by many chemists. Yet in the magnitude of its effects it usually far exceeds the correction for compression, since evacuation involves the removal of a pressure equivalent to a head of about 30 feet of water, while the compression involves usually the addition of only a few inches. The following observations show that, in point of fact, the effect cannot be ignored in any but the roughest work.

---

[1] Young, Stoichiometry (London), 1908), 264.

[2] Since the above was written, a single, inconspicuous instance has been noticed.

Experiments.—Eleven thermometers (mercury in glass) of various makes were selected. Seven were graduated in tenths of a degree, and were capable of being read to hundredths. Two (Nos. 9 and 10) were graduated in fifths, and two (Nos. 1 and 11) in hundredths of a degree. The thermometers, fitting tightly through rubber stoppers, were partially enclosed in test tubes, provided with side tubes. The tubes were supported in a thermostat, the temperature of which remained constant ±0.005. After the reading of each thermometer became constant, the test tube was exhausted to 20 mm. through the side tube, and the new reading, after constancy was reached, was taken. Air was then re-admitted, and the readings were repeated, to ascertain that no permanent change in the value at one atmosphere pressure (or more exactly 748 mm.) had occurred.

The results are given in the table. The diameters of the bulbs are outside measurements (mm.). The thickness of the glass of the bulbs differed considerably, but could not, of course, be measured. Nos. 9 and 10 were members of a set of Anschütz thermometers. No. 4 was of Jena normal glass, by Götze:

	Bulb.		
No.	Length	Diam.	Change.
1	58	5.0	0.144°
2	28	6.5	0.16
3	25	5.0	0.13
4	20	5.5	0.10
5	20	5.0	0.13
6	9	5.5	0.11°
7	9	5.5	0.11
8	10	5.0	0.10
9	10	4.2	0.14
10	10	4.2	0.17

The change in apparent temperature (dilatation) varied from 0.10 to 0.17°. Considering the very great differences in the sizes of the bulbs, it was surprising that the changes did not cover a wider range. Evidently the amount of the effect cannot be predicted from the dimensions of the bulb.

When intermediate pressures were used, the change, as might be expected, was found to be a linear function of the pressure.

Only one of the eleven thermometers suffered a permanent distortion. In this case (No. 11) the bulb measured 35 x 9.5 mm. The successive values of the change were 0.260°, 0.177°, 0.162°, 0.162° (constant).

Conclusions.—(1) In vacuum distillation, if the temperatures are to be reasonably correct, special investigation of the behavior of each thermometer is required. In view of the behavior of our eleven thermometers, which showed no relation to the size of the bulb, an error much greater than 0.2° might be involved in the case of an individual instrument.

(2) In measurements of vapor pressures, by methods in which the bulb of the thermometer is immersed in the vapor, an error of 0.15°

or more may exist in the temperature readings. The absence of any correction on this account vitiates many of the published data. Specific instances will be noted in later papers dealing with vapor pressures.

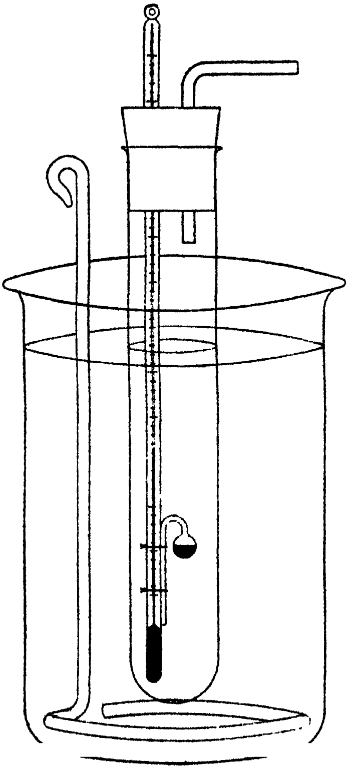
[COMMUNICATION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

STUDIES IN VAPOR PRESSURE: II. A SIMPLE DYNAMIC METHOD, APPLICABLE TO BOTH SOLIDS AND LIQUIDS, FOR DETERMINING VAPOR PRESSURES, AND ALSO BOILING POINTS AT STANDARD PRESSURES.

BY ALEXANDER SMITH AND ALAN W. C MENZIES.

Received June 11, 1910.

The principle of the submerged bulblet method of determining boiling points, described in the preceding paper, may be adapted to the measurement of vapor pressures. The necessary apparatus may be set up from materials found in any laboratory, and a series of measurements of considerable accuracy may be made, all with the expenditure of very little time.



The Apparatus.—The bulblet, with attached capillary tube not less than 1 mm. in diameter, is charged with a small amount (about 0.1 g.) of the solid or liquid substance, and is attached to the thermometer by means of thread or asbestos cord, just as for the boiling-point determination. Instead, however, of being then immersed directly in the open bath, it is enclosed in a test tube (see figure). The L-shaped tube leads to the manometer, connections with the atmosphere and with a pump being provided by means of T-tubes. A large bottle between the pump and manometer is useful for regulating the pressure. Stopcocks on the tube leading to the pump and on that opening to the air permit the pressure to be lowered or raised at will. For pressures below that of the atmosphere, a water-pump, and for pressures above that of the atmosphere a small compression pump (*e. g.*, a bicycle pump) may be used. With only a rubber stopper closing the test tube, the pressure cannot be carried far above that of the atmosphere. But this apparatus will serve well when direct observation of the boiling point at standard pressure (760 mm.) is desired.

The test tube contains the same liquid as the surrounding bath. What was said in the first paper in regard to suitable bath liquids (p. 899), and in regard to the choice of thermometers (p. 902) applies here. The bath may be stirred by hand.

The Manipulation.—It will be sufficient to describe the mode of operation when pressures below that of the atmosphere are being observed. After the temperature has become constant at the desired point, and time has been allowed for equalization of the temperatures within and without the test tube, the pressure is reduced by cautiously opening the stop-cock on the tube leading to the pump. When the pressure has fallen to, or just below, the vapor pressure of the solid or liquid, a continuous stream of bubbles issues from the capillary. In a few moments, the vapor of the substance has displaced the air in the bulb, and usually also all the oxygen, nitrogen, or moisture dissolved in the substance, or adhering to the substance or the glass. The stop-cock on the tube leading to the pump is now closed, and that admitting air is slightly opened. The pressure is allowed slowly to rise until the stream of bubbles ceases. Use of the stop-cock alone does not permit of fine adjustment. Admission of air, a very little at a time, is best effected by grasping and closing the rubber tube at two places with the fingers. The volume of air in the enclosed section of the tubing bears only a small ratio to the total volume of the apparatus, including the bottle. By opening and closing the two constrictions alternately, first that next to the apparatus, then that nearer to the end which is open to the atmosphere, air is admitted in minute amounts at a time, and the pressure is raised very gradually. When the stream of bubbles suddenly ceases, the pressure of the air in the apparatus is equal to that of the vapor. The pressure at this moment is read on the manometer. This method applies when the substance and bath liquid are mutually insoluble. When they are mutually soluble, the bath liquid is allowed to ascend to a predetermined point, 5–10 mm. from the mouth of the capillary, just as in the boiling-point determination (p. 900).

To make sure that the dissolved or adhering gases and moisture are all expelled, the pressure is lowered, and the boiling out and subsequent operations are repeated. If consecutive measurements do not finally give constant values at the same temperature, the substance is impure, either because of original impurity or of decomposition during the heating. When a satisfactory reading has been obtained, the temperature is raised 5° or 10° and the same operations are carried out at the new temperature. If an open manometer is used, the barometric height (reduced to mercury at 0°) is taken also, and the reading of the manometer (likewise reduced to 0°) is subtracted from it.

A correction for the pressure, due to the depth from the surface of the bath down to the mouth of the capillary, or to the point to which the liquid ascends, is required. The details of this correction are identical with those described in the paper on boiling points (p. 901).

Sample Determination: Water.—To illustrate the adaptability of this form of the submerged bulblet method to securing quickly and easily a series of measurements of moderate accuracy, the results with water may be given. The test tube and bath were filled with mineral oil. Elaborate precautions to insure accuracy were purposely avoided. The manometer consisted of a piece of glass tubing fastened rigidly to an ordinary wooden meter scale. It stood in a vessel of mercury. Correction was made for capillarity in the manometer (+1.7 mm.), and the readings of the manometer and barometer were reduced to mercury at 0°. The correction for the immersed depth of the bulblet was made. One of a set of short Anschütz thermometers graduated in fifths of a degree was used, and the thread was completely immersed. Comparison with a standard thermometer showed no errors over 0.05°, and the readings were therefore assumed correct. The following were the observed readings, after correction:

Temp.	V. p. S and M.	V. p. H & H.	Diff. mm.	Temp.	V. p. S and M.	V. p. H & H.	Diff. mm.
49.0	88.0	[87.8]	+0.2	80.0	355.4	355.1	+0.3
60.7	155.3	154.1	+1.2	85.5	441.5	442.2	—0.7
67.8	213.8	212.2	+1.6	90.0	526.5	525.8	+0.7
73.6	273.5	272.5	+1.0	95.3	640.5	641.1	—0.6

The columns H & H contains the values published by Holborn and Henning,[1] which are the most trustworthy available. The algebraic sum of the differences divided by the number of observations gives the divergence of the curve as a whole from that of H & H. This divergence is 0.46 mm, and the corresponding divergence of the temperature is 0.07°.

This arrangement was used successfully in preliminary measurements of the vapor pressures of mercury and of non-fusing solids like the mercurous halides at 280–370°.

Three Additional Sources of Error, and the Corrections Therefor.—The irregularity of the individual observations cited above is due to the crudeness of the manometer, chosen intentionally to avoid the use of any special apparatus. Aside from this, however, there are three other sources of error for which, if desired, correction may be made.

---

[1] *Ann. Physik*, [4] 26, 882 (1908).

. One of them is the error due to neglecting the pressure caused by capillary ascension of the bath liquid in a tube 1 mm. in diameter. As we have shown,[1] this involves an error of only about 1 mm. of mercury pressure, or usually about 0.04° in temperature. In the case of the paraffin oil used in the foregoing determinations, this error was only 0.5–0.6 mm. Unless, therefore, the temperature is being read with unusual precautions, this correction may be ignored.

The second source of error lies in the fact to which attention is called in a separate communication,[2] namely, that a thermometer bulb placed in a partial vacuum undergoes dilatation and gives low readings.

The amounts of these two corrections, and the effect of taking account of them, is shown with the same data in the following table:

Temp.	V. p. S and M.	Temp. corr. for dilatation	V. p. change per 1°.	Corr. for dilatation in mm.	Corr. for capil. in mm.	S and M corr.	Diff. from H & H.
49.0°	88.0	0.13°	4.5	—0.6	+0.6	88.0	+0.2
60.7	155.3	0.11	7.1	—0.8	+0.6	155.1	+1.0
67.8	213.8	0.10	9.2	—0.9	+0.6	213.5	+1.3
73.6	273.5	0.09	11.5	—1.0	+0.6	273.1	+0.6
80.0	355.4	0.08	14.6	—1.2	+0.5	354.7	—0.4
85.5	441.5	0.06	17.3	—1.0	+0.5	441.0	—1.2
90.0	526.5	0.04	20.0	—0.8	+0.5	526.2	+0.4
95.3	640.5	0.02	23.4	—0.5	+0.5	640.5	—0.6

By these corrections, the divergence from the standard values is reduced from 0.46 mm. to 0.16 mm., or, in temperature, from 0.07° to 0.03°.

It will be seen that these two corrections work in opposite directions. On this account, when the present apparatus is used for securing a series of approximate vapor pressures, and for the applications to be mentioned presently, they may be neglected. When accurate vapor pressure measurements are required by a dynamic method, a modified, less simple form of the apparatus, to be described in a later paper, may be employed with advantage. In this apparatus, one of these corrections (that for dilatation) disappears, and the other is therefore to be taken into account.

The pressures may be still further corrected for the value of the gravity constant at the place of observation. In this laboratory the correction is —0.25 mm. per 760 mm. This correction, if applied, reduces the average divergence of the curve of pressures observed from the standard curve to 0.06 mm., or about 0.01°. This final result shows that by the method results of remarkable accuracy are obtainable.

Application to the Determination of Boiling Points of 760 mm., and under Reduced Pressure.—The present, almost universal custom of publishing boiling points at whatever atmospheric pressure happens to exist at the time, aggravated in the majority of cases by omission to state what that pressure was, raises some question as to the carefulness of the whole investigation, and, besides, tends to defeat the purpose for which ostensibly such data are given, namely the identification of substances. Thus, even when the barometric height is only 16 mm. distant from 760 mm., the boiling point of alcohol is 0 5° in error and that of naphthalene no less than 1°. It is extremely desirable that uniformity should be observed, and that all boiling points of stable substances should be ascertained at the normal pressure of 760 mm., and published in that form. The submerged bulblet method just described renders this operation so easy that the added value of the data is worth far more than the little extra trouble involved.

---

[1] See first paper, THIS JOURNAL, 32, 902.

[2] See preceding paper, THIS JOURNAL, 32, 906.

When the substance is unstable at its boiling point, and has been purified by distillation under a reduced pressure, the boiling point at this pressure is published, and in such cases the value of the pressure is usually given. Commonly, to promote quiet boiling, a fine stream of air enters the boiling liquid through a capillary. Examination of the literature shows conclusively, however, that boiling points determined in this way are utterly untrustworthy.

This was clearly exhibited, for example, in connection with the controversy[1] over the question of whether such a boiling point was identical with the temperature at which the substance exercised a vapor pressure equal to that used in the distillation. Employing a vacuum distillation apparatus of the standard type, but more carefully constructed than the forms commonly used, G. W. A. Kahlbaum[2] found the boiling points to be sometimes higher and sometimes lower. The differences were, indeed, finally demonstrated to be in part due to the fact that the vapor pressure observations which he chose for comparison were inaccurate.[3] In at least one conspicuous case (butyric acid), also, the material was very impure.[4] But the greater part of the differences was due simply to the form of this particular apparatus, which was never devised for obtaining exact boiling-point-pressure readings. The original, and still, practically, the only purpose of the apparatus is to secure efficient purification by fractionation *in vacuo*. Any form which will achieve this end may be used, and is used.

To illustrate the striking differences between boiling points in a distillation apparatus and the true boiling points under various pressures, as determined in an apparatus especially devised for this purpose, a few typical values are given below. In the columns headed K appear Kahlbaum's[1] boiling points. The substances, in these instances, could not have been seriously impure. Under R & Y and Y are given the boiling points as ascertained by Ramsay and Young and by Young, respectively, and these results are confirmed by other published data.

---

[1] List of references, Ostwald, *Handb.*, 1, 308, to which add *Z. physik. Chem.*, 7, 438, and *Z. physik. Chem.*, 6, 594.

[2] *Ber.*, 16, 2476.

[3] Ramsay and Young, *Ibid.*, 19, 2114.

[4] Bannow, *Ibid.*, 19, 2552.

Pressures. mm.	Benzene.		Ethyl alcohol		Bromobenzene.		Aniline		Quinoline.	
	K.	R & Y.[2]	K.	R & Y[3]	K.	R & Y.[2]	K.	R & Y.[4]	K.	Y.[5]
5	—0.6	..	+1.5	...	29.8	28.5	65.5	..	97.2	89.5
10	+1.3	..	6.5	—2.85	41.5	40	72.7	...	106.6	104
15	3.3	—10	9.5	+2.80	49.6	47.5	78.3	...	112.6	113
20	5.1	— 5	12.4	7.35	55.8	53.5	83.0	81.5	118.0	120
25	6.4	— 1	14.4	10.75	60.1	58	87.2	86	121.9	125
50	13.8	+12	23.5	22.15	70.7	73.5	100.9	102	136.5	142
75	20.1	+20.5	29.0	29.20	77.3	83	108.2	112.5	144.8	154

The especial unfitness of the distillation apparatus at low pressures, where the temperature is below that of the room, is shown particularly in the cases of alcohol and benzene. Here, heat reaches the thermometer by radiation faster than it can be removed by a vapor of low heat capacity, and the temperatures are all much too high. Kahlbaum[6] states that wrapping cotton round the bulb, whether this cotton is previously moistened with the substance or not, does not, in these cases, bring about better correspondence of the results.

Quite recently, Von Rechenberg[7] has called attention to another error due to the fact that the large amount of vapor passing through the distillation apparatus gives a steep pressure gradient between the flask and the pump. When the manometer is distant from the flask, the observed pressure may be as much as 12 mm. below that existing in the flask. When air is admitted freely through a capillary to prevent "bumping," the steepness of this gradient is higher than it would otherwise be.

It seems, therefore, to be desirable that the boiling points (and corresponding pressures) of substances isolated by vacuum distillation should always be determined by a measurement made especially for the purpose. The submerged bulblet method described above furnishes a simple apparatus, and gives results of the requisite degree of accuracy. It is free from the error due to the air entering through the capillary. This method involves in reality a distillation *in vacuo*, but the extremely small amount of actual vapor transference occuring completely obviates the source of error noted by Von Rechenberg. The method avoids the error at low temperatures due to superheating of the thermometer by radiation, as the latter is immersed in a bath liquid of great heat capacity. It eliminates also, for the same reason, all the variability in the conditions, and therefore in the results, to which, as we have seen,[1] the distilling flask method is liable.

---

[1] *Ber.*, 17, 1259.

[2] *J. Chem. Soc.*, 55, 501–3.

[3] *Ber.*, 18, 2856.

[4] *J. Chem. Soc.*, 47, 649.

[5] *Ibid.*, 55, 485.

[6] *Ber.*, 19, 947.

[7] *J. prakt. Chem.*, 79, 475. For further discussion of this subject see Kraffts, *Ibid.*, 2, 80, 242 (1909); Hansen, *Ibid.*, 80, 449; Krafft, *Ibid.*, 80, 469; and the reply of von Rechenberg, *Ibid.*, 80, 547. Also Siepermann, *Ibid.*, 81, 190; and Hansen, *Ibid.*, 81, 282.

For data which are to be published, ready comparability would be secured by choosing a list of predetermined pressures, such as 5, 10, 20, 50, 75, 100, 200 mm., etc., up to 760 mm., the particular pressures being selected from this list with reference to the stability of the substance. The simplest way to accomplish this is to make several vapor-pressure readings in the desired region, to prepare a temperature-pressure curve from the data, and to read off the temperature at the exact pressures selected.

Reduction of Boiling Points to 760 mm. by Calculation.—It does not seem to be widely known that the observed boiling point at existing atmospheric pressure may be reduced to the value at 760 mm. by calculation alone, and usually without serious error. A rule given by Landolt,[2] which appears to be the only one that is familiar, is to the effect that the boiling point changes 0 043° for each mm., or, what is the same thing, 1° for every 23.3 mm. Now the following changes in pressure for 1° at the boiling point show this statement to be too inexact for practical use: Benzene, 24 mm.; ether, 27 mm.; alcohol, 30.3 mm.; naphthalene, 17 mm.; mercury, 13.6 mm.; water, 27.2 mm. Landolt's rule in reality overlooks the fact that the change in pressure per 1° is not constant, but varies inversely with the boiling point on the absolute scale. The following rule, based on the Clausius-Clapeyron law, and identical with, but simpler in form than that of Young,[3] gives results of accuracy sufficient for many purposes: *Divide 8500 by the boiling point on the absolute scale* (observed at about one atmospheric pressure), *and the quotient is the change in pressure (in mm.) for 1° change in boiling point.*

The constant varies, changing by about 1 per cent. for every 10 mm. below or above 760. The above value (8500) can be used, therefore, only for observed boiling points near to 760 mm. This value applies to most substances, but for alcohols, acids, water, and other substances containing the hydroxyl group the value 10200 must be used instead. The following data illustrate the degree of approximation attained by the use of this rule:

---

[1] See first paper, THIS JOURNAL, 32, 897.

[2] *Ann.* (Liebig), *Suppl.*, 6, 175.

[3] *J. Chem. Soc.*, 81, 777. The number 8500 is the reciprocal of Young's constant, *c*.

	B.-p. C.	B.-p. abs.	V. p. change. obsd. mm.	V. p. change. calc. mm.
Benzene	80°	353°	24	24.1
Naphthalene	218	491	17	17.3
Chloroform	62	335	25.2	25.4
Carbon disulphide	46	319	24.7	26.6
Aniline	184	457	19.5	18.6
Methyl acetate	57.5	330.5	26.8	25.7
Methyl formate	32.3	305.3	28.8	27.8
Amyl *n*-butyrate	178.6	451.6	19	18.8
Ether	34.6	307.6	27	27.6
Mercury	357	630	13.6	13.5
Sulphur	445	718	12.2	11.8
Water	100	373	27.2	27.3[1]
Alcohol	78.4	351.4	30.3	28.9[1]
Acetic acid	119	392	24	26.0[1]

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 52.]

THE CONDUCTANCE AND IONIZATION OF POTASSIUM TRI-IODIDE, AND THE EQUILIBRIUM BETWEEN IODINE, IODIDE, AND POLYIODIDES IN AQUEOUS SOLUTION.

BY W. C. BRAY AND G. M. J. MACKAY.

Received June 13, 1910

This investigation was undertaken in order to determine the equivalent conductance of the tri-iodide ion, I_3^-; for a knowledge of this quantity is needed in the study of the equilibrium between iodine, iodide, and polyiodides in aqueous solution. Our own experimental work deals only with dilute solutions; but so much experimental evidence relating to this equilibrium in more concentrated solutions is available that it has seemed worth while to consider the results of several of these investigations from a single point of view. Accordingly, after presenting our own results, we have attempted to calculate the proportion of iodide, tri-iodide, and higher polyiodide present in a normal KI solution saturated with iodine.

The only careful determination of the conductance of tri-iodide ion, Λ_{I_3}, is that of Burgess and Chapman,[2] who calculated, from transference experiments, that $\Lambda_{I_3}/\Lambda_I = 0.566$. If we accept the value $\Lambda_I = 76.5$ at 25°, as given below, then Λ_{I_3} is found to be 42.5. We have recalculated these results[3] and have found the same mean value for Λ_{I_3}, although the separate values do not agree perfectly with the original calculations. These experiments are, it is true, open to the objection that concentration changes are referred to a constant volume of solution instead of to a definite weight of water. But we have estimated, on the assumption that the partial volume of 1 gram of dissolved iodine (as explained below) is 0.2376 cc. and that of 1 gram dissolved potassium iodide is 0.283 cc., that the error introduced in this way is less than 0.2 per cent.

---

[1] Constant here 10200, for the others 8500.

[2] Burgess and Chapman, *J. Chem. Soc.*, 85, 1305 (1904).

[3] The share of transport of tri-iodide ion, $C_{I_3^-} \times \Lambda_{I_3}/(C_{I_3^-} \times \Lambda_{I_3} + C_{I^-} \times \Lambda_I + C_{K^+} \times \Lambda_K)$ equals $\frac{1}{2}(B/A - 1)$ and may be obtained directly from the values of B/A given by these authors in the table on page 1316. The concentration ratio $C_{I^-}/C_{I_3^-}$ is given as C_2/C_1 in the tables on page 1309, the degrees of ionization of KI and KI_3 being assumed equal.

The method which we have used in determining Λ_{I_3} depends upon the measurement of the change of conductance produced by dissolving iodine in a solution of potassium iodide. A few incidental measurements of this kind have been made by LeBlanc and Noyes[1] and by Burgess and Chapman,[2] from which the last named authors calculated that the average value of the ratio Λ_{I_3}/Λ_I is 0.553. This close agreement with the results of their transference experiments is purely accidental; for the individual values (eight in all) derived from the conductance measurements vary irregularly between 0.51 and 0.60, corresponding to a variation of Λ_{I_3} between 39 and 46. The inaccuracy of these measurements is doubtless due to the fact that the amount of KI_3 present was much smaller than that of KI. We have avoided this source of error as far as possible by saturating the KI solution with iodine, and thus obtaining a concentration of KI_3 nearly equal to that of the uncombined KI.

The fundamental assumption which is made in interpreting any of these experimental results is that the only polyiodide present is KI_3. This depends upon the measurements of the equilibrium $I_3^- = I^- + I_2$ made by Jakowkin[3] at 25° and Dawson[4] at 13.5°, in which the concentration of I_2 as such in the aqueous solution was varied and determined by partition experiments, and the additional dissolved iodine was assumed to be present as KI_3. The values of the equilibrium constant[5]

$$K = \frac{(I_2)(I^-)}{(I_3^-)} = \frac{C_{I_2}\gamma C_{\Sigma I}}{\gamma' C_{\Sigma I_3}}$$

could not be directly determined but the values of the expression

$$K_1 = \frac{C_{I_2}C_{\Sigma I}}{C_{\Sigma I_3}}, \text{ where } K = \frac{\gamma K_1}{\gamma'}$$

We have also assumed that Λ_K at 25° = 74.8, and that $C_{\Sigma I}C_{I_2}/C_{\Sigma I_3}$ = 0.00138. The values of Λ_{I_3} calculated from the separate experiments, and given in the same order as on page 1309, are 42.3, 42.9, 42.6, 42.5, 41.9, 42.4, and 43.3.

[1] LeBlanc and Noyes, *Z. physik. Chem.*, 6, 402 (1890).

[2] Burgess and Chapman, *Loc. cit.*, 1310.

[3] Jakowkin, *Z. physik. Chem.*, 20, 19 (1896).

[4] Dawson, *J. Chem. Soc.*, 79, 238 (1901).

[5] Concentrations are represented by means of parentheses, or by the letter *C*. $C_{\Sigma I}$ means the total concentration of iodide. γ and γ' are the degrees of ionization of KI and KI_3 respectively.

were found to be remarkably constant when the concentrations of I_2, KI and KI_3 were greatly varied. We have collected in the following table some additional values of K_1 at 25° which we have calculated from the experimental data of Maitland.[1] A few of Jakowkin's results are also presented for comparison. The first column shows the concentration in mols per liter of the total potassium salt present, $C_{\Sigma K} = C_{\Sigma I} + C_{\Sigma I_3}$. The values of K_1 and the corresponding values of C_{I_2} are arranged in horizontal rows:

TABLE I.—VALUES OF $K_1 = C_{I_2}C_{\Sigma I}/C_{\Sigma I_3}$ AT 25°.

$C_{\Sigma K}$.					
0.0625	$C_{I_2} \times 10^4$	0.754	1.59	5.71	Jakowkin
	$K_1 \times 10^3$	1.38	1.40	1.41	
0.100	$C_{I_2} \times 10^4$	0.453	1.855	4.190	Maitland
	$K_1 \times 10^3$	1.39	1.38	1.36	
0.200	$C_{I_2} \times 10^4$	0.474	1.179	4.02	Maitland
	$K_1 \times 10^3$	1.41	1.39	1.35	
0.400	$C_{I_2} \times 10^4$	...	1.33	...	Maitland
	$K_1 \times 10^3$	...	1.32	...	
0.500	$C_{I_2} \times 10^4$	0.541	1.114	3.60	Maitland
	$K_1 \times 10^3$	1.37	1.33	1.27	
1.00	$C_{I_2} \times 10^4$	0.484	1.013	2.904	Maitland.
	$K_1 \times 10^3$	1.30	1.26	1.08	

It is evident that Maitland's results are in good agreement with those of Jakowkin, and that in the dilute solutions the amount of polyiodides higher than KI_3 must be extremely small. In the concentrated KI solutions, however, the values of K_1 are smaller and show a steady decrease with increasing concentration of I_2.[2]

The expression K_1 is related to the equilibrium constant K by the equation $K = (\gamma/\gamma')K_1$, where γ and γ' are the degrees of ionization of KI and KI_3, respectively. Dawson concluded from the constancy of K_1 that $\gamma = \gamma'$, but this is not necessarily true. It has been found, from conductance measurements, that in a mixture of two salts with a common ion the degree of ionization of each salt depends only on the total ion concentration and for highly ionized salts changes only very slowly with the ion concentration. Since, moreover, the degrees of ionization of KI and KI_3 do not differ greatly, it follows that the degree of ionization of potassium iodide, γ, will not be changed appreciably when a portion of it is converted into tri-iodide by dissolving iodine in its solution, and that also, in the different solutions which may be prepared from a given potassium iodide solution, the degree of ionization of KI_3 will have a definite, constant value, γ'.[3]

---

[1] Maitland, *Z. Elektrochem.*, 12, 264 (1906).

[2] This will be considered later; the corresponding values of K_1 for solutions saturated with I_2 are given in Table V, γ' being then assumed equal to γ.

[3] This conclusion, that for such a series of solutions γ/γ' is a constant, was reached

Upon the basis of the conclusion that the ionization γ of KI is unchanged by the addition of iodine, the results of our conductance measurements may be represented by the following equations, where L and L' represent respectively the specific conductances of the potassium iodide solution and of the same saturated with I_2:

$$1000\,L = \gamma C_{\Sigma I}\,(\Lambda_K + \Lambda_I)$$

$$1000\,L' = \gamma C'_{\Sigma I}\,(\Lambda_K + \Lambda_I) + \gamma' C'_{\Sigma I_3}\,(\Lambda_K + \Lambda_{I_3}).$$

Furthermore, since the change of volume on dissolving the iodine is negligible in dilute solutions we have:

$$C_{\Sigma I} = C'_{\Sigma I} + C'_{\Sigma I_3}.$$

For the simple case that $\gamma = \gamma'$ the difference between the two conductances then becomes:

$$1000\,(L - L') = \gamma C'_{\Sigma I_3}\,(\Lambda_I - \Lambda_{I_3});$$

for the general case, however, the difference assumes the form

$$1000\,(L - L') = (\gamma - \gamma')\,C'_{\Sigma I_3}\,(\Lambda_K + \Lambda_I) + \gamma' C'_{\Sigma I_3}\,(\Lambda_I - \Lambda_{I_3}).$$

Since $\gamma - \gamma'$ approaches zero with decreasing concentration, the two expressoins will become identical at the limit. In other words, if we calculate the difference between the conductances, $\Lambda_I - \Lambda_{I_3} = \frac{1000(L - L')}{\gamma C'_{\Sigma I_3}}$ assuming as a first approximation that $\gamma = \gamma'$, then the limiting value approached in dilute solutions will be a true measure of $\Lambda_I - \Lambda_{I_3}$. We have therefore made a series of determinations in which the initial potassium iodide concentration was varied from 0.1 to 0.001 normal in order to obtain the limiting value of the ratio 1000 $(L - L')/(I_3^-)$.

Preparation of the Substances and Solutions.

The *potassium iodide* solutions, 0 1 and 0.01 normal at 25°, were made by dissolving the requisite amount[1] of the pure salt (Kahlbaum's guaranteed reagent), powdered and dried to constant weight, and diluting (at 25°) to 2 liters. The remaining solutions were prepared from these by dilution by means of a calibrated 200 cc. pipette and a series of calibrated measuring flasks. The strength of the two stock solutions was checked to within 0.1 per cent. by liberating the iodine and titrating

by Osaka (*Z. physik. Chem.*, 38, 743 (1901)), but he made the assumption that the law of mass action could be applied to the ionization of these two salts. Osaka found in his preliminary measurements of the freezing points of 0.5–1.0 normal solutions of potassium iodide before and after adding iodine that after the addition of iodine the freezing point is distinctly higher than before, and concluded that KI_3 is somewhat less ionized than KI. But since the behavior of these concentrated solutions is in general so different from that of more dilute solutions it is not justifiable to conclude that in dilute solutions the degree of ionization of KI_3 is less than that of KI.

[1] The International Atomic Weights of 19.08 were used. No correction, however, was applied for buoyancy.

it by a method to be described in a subsequent paper, thus proving the absence of chloride or other impurity.

The *water* used was prepared by redistilling ordinary distilled water from an alkaline solution of potassium permanganate; it had a specific conductance of from 0.4 to 0.8 × 10^{-6} reciprocal ohms at 25°. The conductance of the water was in each case subtracted from the conductance of the weaker solutions.

The *sodium thiosulphate* solution used in titrating "free iodine" in the three more concentrated solutions was 0.07348 normal. It was standardized by comparison with an iodine solution which had been titrated against a weighed quantity of As_2O_3 according to the directions of Washburn.[1] For the titration of the more dilute iodine solutions this standard thiosulphate solution was diluted just before use to five times its volume.

The *iodine* used was obtained by purifying commercial resublimed iodine. This was ground with about one-quarter of its weight of potassium iodide and carefully sublimed; the iodine thus obtained was again sublimed without the addition of any potassium iodide.

The Experimental Method.

The *conductance measurements* were made in glass cells of the pipette form, such as have been described in another article from this laboratory.[2] Two were used, one of low resistance for the very dilute solutions, and the other of high resistance for the more concentrated solutions. The cell constants were determined by measuring in the cells at 25° freshly prepared solutions of potassium chloride 0.01 normal at 18°, the specific conductance of which was assumed to be 1413 × 10^{-6} at 25°.[3] The measurements were made in the usual way by means of an accurately calibrated bridge of the Kohlrausch roller pattern.

The *saturated solutions* were prepared as follows: Ten to thirty grams of freshly powdered iodine were placed in a 250 or 500 cc. glass-stoppered bottle of "Resistenz" glass, which had been well steamed out. After washing this iodine with a small quantity of a potassium iodide solution the bottle was filled with a potassium iodide solution of the same concentration, the stopper and neck of the bottle were carefully covered with a rubber tube, the bottles were rotated in a thermostat at 25° for different lengths of time, and finally were hung in the thermostat for a few minutes to allow the iodine to settle.

Portions of the saturated solution were forced by air pressure through a glass tube into the conductivity vessel, which was also immersed in the thermostat; and the conductance was quickly measured. Fresh portions of solutions were then forced into the cell in order that the measurement might be checked.

---

[1] Washburn, This Journal, 30, 31 (1908).

[2] Abbott and Bray, This Journal, 31, 732 (1909).

[3] This value is based upon recent measurements made in this laboratory by A. C. Melcher and by F. L. Hunt.

Other portions of the same solution were withdrawn by pipettes of known volume, run into solutions of potassium iodide, and the free iodine titrated with thiosulphate. In filling a pipette the solution was forced by means of air pressure through a filter of glass wool and asbestos connected with the pipette by a ground glass joint. This use of air pressure in transferring the saturated solutions prevented the error from evaporation of iodine which would have arisen if suction had been used. To avoid this error the measurements were also made as quickly as possible and only one-half, or at most two-thirds, of the solution in the bottle was used.

The Conductance and Solubility Data.

All the experimental data are presented in the following table:

TABLE II.

KI solution			KI solution saturated with iodine			Best values	
Milli-mols per liter	Equiv cond.	Spec cond. $\times 10^6$	Hours rotation.	Spec cond 10^6.	Milli-mols I_2 dissolved.	Spec cond. $\times 10^6$.	Total iodine dissolved.
100	130.8	13080	25	11500	51.1	11490	51.35
	130.8	13080	120	11485	51.6		
50	134.75	6737.5	25	5930	25.77	5930	25.77
20	139.4	2788	25	2468	11.13	2468	11.13
10	142.2	1422	20	1259	6.185	1260	6.185
	142.4	1424	54	1261	6.080[1]		
5	144.5	722.5	20	641.0	3.725	641	3.728
	144.8[1]	724.0[1]	54	642.0[1]	3.731		
2	147.0[1]	294.0[1]	4	260.2	2.292[1]	260.8	2.266
	146.7	293.4	20	260.8	2.266		
	146.6	293.2	54	261.2	.....		
1	149.95	147.95	4	131.6	1.772	131.7	1.788
	147.9	147.9	20	131.9	1.788		
	148.0	148.0	48	131.8	1.793		
	147.8	147.8	54	133.2[1]	1.787		

It will be seen that the duplicate measurements of conductance gave concordant results throughout, but the values of "iodine dissolved" in the saturated solutions are somewhat less satisfactory. The maximum variation from the mean is 1 per cent. in the most dilute solution, 0.5 per cent. in the most concentrated, and 0.1 per cent. in an intermediate solution (0.005 mol. KI).

The Equivalent Conductance of Potassium Iodide.

A comparison of the conductance data presented above with those obtained by earlier investigators is afforded by Table III. This contains values interpolated from the results at 25° of Ostwald,[1] of Jones and Douglas[2] and Schmidt and Jones,[3] all reduced from Siemann's units to reciprocal ohms by multiplying by 1.066. Values at 25° derived by combining the data of Kohlrausch and Steinwehr at 18° with Déguisne's temperature coefficients[4] and making a slight correction for the expansion of the solution are also included. The table also contains in the last two columns the percentage ionization of potassium iodide at 25° and at 18° derived from our data and those of Kohlrausch, respectively. These columns serve to show the consistency of the data at the two temperatures and the very small effect of temperature on the ionization.

---

[1] These data were rejected in deriving the best values because they were not consistent with the data at other concentrations.

TABLE III.—EQUIVALENT CONDUCTANCE AND PERCENTAGE IONIZATION OF POTASSIUM IODIDE.

	Λ for KI at 25°.					100γ for KI.	
Concentration.	Bray & MacKay.	Ostwald.	Jones & Douglas.	Schmidt & Jones.	Kohlrausch & Déguisne	(25°).	(18°).
0.1	130.8	...	128.8	133.9	...	86.5	86.95
0.05	134.7	...	133.0	136.7	134.9	89.1	89.45
0.02	139.4	139.3	139.3	140.3	...	92.1	92.30
0.01	142.3	143.1	142.7	142.4	...	94.1	94.20
0.005	144.5	146.2	146.0	144.8	...	95.5	95.60
0.002	146.7	148.7	149.1	146.8	...	97.0	97.05
0.001	147.9	150.0	150.3	148.3	147.9	97.8	97.85
0.0	151.3	...	...	...	...	100.0	100.00

In the last row of the table is given the equivalent conductance at zero concentration. To derive this we have employed a method which has already been described in several publications from this laboratory,[5] which consists in plotting values of $1/\Lambda$ against the corresponding values of $(C\Lambda)^{n-1}$ for different values of *n*. For the sake of comparison the results of Kohlrausch and Steinwehr on potassium iodide at 18° were plotted on the same diagram. It was found that in both cases a straight line was obtained between the concentrations 0.001 and 0.02 normal for the value $n = 1.45$; that the line expressing the results at 18° met the $1/\Lambda$ axis at a point corresponding to $\Lambda = 131.1$, identical with the value of Λ_0 chosen by Kohlrausch and Steinwehr; and that in the case of the results at 25° the corresponding value of Λ_0 is 151.3 ± 0.1. These results show that between the concentrations 0.001 and 0.02 the dilution law takes the form $(\gamma C)^{1.45}/C(1-\gamma) = \text{const.}$ At higher concentrations a lower value of *n* than 1.45 must be chosen.[6] This graphical method has also shown that our individual measurements are consistent with one another, and that the lower value (144.5) found for the equivalent conductance of the 0 005 normal solution is more nearly correct than the higher value (144.8).

---

[1] Landolt-Börnstein-Meyerhoffer, Tabellen, p. 748.

[2] *Am. Chem. J.*, 26, 445 (1901).

[3] *Ibid.*, 42, 73 (1909).

[4] Landolt-Börnstein-Meyerhoffer Tabellen, p. 744 and 755.

[5] See for example THIS JOURNAL, 31, 745 and 1010 (1909).

[6] The conductance measurements at 18° for solutions more dilute than 0.001 normal indicate that *n* has a higher value than 1.45 in these very dilute solutions, and

It will be seen that the two conductance values of Kohlrausch and Déguisne agree almost completely with ours, and that the ionization values at 18° and 25° run closely parallel, those at 18° being uniformly slightly higher and by an amount that increases gradually as the concentration increases. The results of Ostwald and of Jones and Douglas agree with ours only at 0.02, being considerably higher at the lower concentrations, owing probably to errors introduced by the method of dilution employed. Those of Schmidt and Jones at the lower concentrations (0.01 to 0.001 normal) are much lower than those of Jones and Douglas and fairly concordant with our values; but at the higher concentrations (0 1 to 0.02) the results of Schmidt and Jones are widely divergent from all the others.

The most probable values of the conductances Λ_I and Λ_K of the separate ions were considered to be 76.5 and 74.8, respectively, the sum of which is of course equal to $\Lambda_0 = 151.3$. These values are based upon some unpublished conductance measurements at 25° which will be discussed in a later publication.

The Equivalent Conductance of Potassium Tri-iodide.

Before the data for the solutions saturated with iodine could be interpreted it was necessary to determine whether any correction should be made for the conductance of iodine in pure water. The results of experiments on the hydrolysis of iodine described in the following article show that the initial conductance of an iodine solution in water is due mainly to the acid formed by the hydrolytic reaction, $I_2 + H_2O = HIO + H^+ + I^-$, and that this hydrolysis is driven back almost completely in the presence of a dilute acid. Since an iodide may be expected to have the same effect, no correction has been made for the conductance of iodine in pure water.

It will also be shown in that article that the solubility of iodine as I_2 is 0.00132 mols per liter—a value that will be used in the following calculations.

To the measured conductances of the more concentrated solutions a small correction must, however, be applied on account of the increase of volume when the iodine is dissolved; for in determining the change of conductance resulting from the transformation of KI into KI_3, it is necessary to compare solutions of the same concentration with respect to potassium. Mr. R. C. Tolman, of this laboratory, has kindly furnished

that therefore the values of Λ_0 chosen at 18° and 25° are somewhat too high. For the sake of uniformity however, we have retained the Kohlrausch value.

us with the results of his preliminary measurements on the specific gravities of solutions obtained by dissolving varying amounts of iodine in a 0.25 normal KI solution. The volume-increase of 1 liter of the potassium iodide solution was found to be 0.2376 cc. per gram of iodine dissolved in it. It was calculated that the total concentration of potassium salts in the three most concentrated solutions saturated with iodine differed from the original round concentrations by 0.31, 0.16 and 0.05 per cent., respectively, thus giving 0.9969, 0.04992 and 0.01999 mols per liter. The specific conductances of pure potassium iodide solutions at the same concentrations were therefore calculated to be 0.013040, 0.006727 and 0 002786, respectively, and these values have been used in determining the decrease of specific conductance (Table IV, column 6).

In Table IV the final results and some quantities calculated from them are presented. Concentrations are expressed in the table in millimols per liter at 25°, but all calculations are based upon molal concentrations. The *first* column gives the total concentration of the potassium salts in the solutions, the values in the three most concentrated solutions having been obtained by correcting the values given in Table II as just described. The *third* column gives the concentration of the tri-iodide ($\Sigma I_3 = I_3^- + KI_3$), obtained by subtracting the solubility of I_2 (1.32) from the "total iodine dissolved," as given in the last column of Table II. The *second* column gives the concentration of iodide (ΣI) determined by taking the difference between the two concentrations just referred to ($\Sigma K - \Sigma I_3$). The *fourth* column gives the concentration of tri-iodide ion, (I_3^-), calculated under the assumption that the degree of ionization of KI_3 is the same as that of KI in the initial KI solution. The *fifth* column contains the ratio $\Sigma I_3/(\Sigma I + \Sigma I_3) = r$. The *sixth* and *seventh* columns show the decrease in specific and equivalent conductance, $L - L'$ and $\Delta\Lambda$, respectively, produced by replacing the iodide by exactly the same amount of tri-iodide. The *eighth* column contains the values of the ratio, $1000\ (L - L')/(I_3^-)$, which should be constant, and equal to $\Lambda_I - \Lambda_{I_3}$, if the ionization of KI_3 is the same as that of KI. The *ninth* column shows the values of the ratio, $\Delta\Lambda/\gamma$, which would equal the decrease of equivalent conductance if all the KI were replaced by KI_3, no assumption in regard to degree of ionization of the KI_3 being involved. The *tenth* column contains the values of Λ_{KI_3} calculated by subtracting $\Delta\Lambda/\gamma$ from the values of Λ_{KI} given in Table III, and the *last* column gives the corresponding values of the percentage ionization of KI_3, $100\gamma_{KI_3}$, calculated on the assumption that Λ_0 for KI_3 is equal to 115.8.

An inspection of the table shows that all the results are concordant except the value $r = (\Sigma I_3)/(\Sigma I + \Sigma I_3) = 4.90$ for the second solution, which is evidently too low. Since this value is based upon only a single titration of "total iodine dissolved," a more probable value, 4.97, has been obtained by interpolation, and the corresponding values of γ_{KI_3}, etc., calculated. These values are enclosed in brackets in the table.

TABLE IV.

Concentrations × 10³.					Decrease in cond.					
$(\Sigma I + \Sigma I_3)$.	(ΣI).	(ΣI_3)	(I_3^-)	$r = \frac{(\Sigma I_3)}{(\Sigma I + \Sigma I_3)}$.	$(L - L')10^6$.	$\Delta\Lambda$	$\frac{1000(L-L')}{(I_3^-)}$.	$\Delta\Lambda/r$	ΛKI_3.	$100\gamma KI_3$
99.69	49.66	50.03	43.28	0.502	1550	15.5	35.8	30.9	99.9	86.3
49.92	25.47	24.45	21.79	0.490	797	15.9	36.6	32.5	102.3	88.3
49.92	...	...	. .	(0.497)[1]	.	. .	(36.0)	(32.0)	(102.8)	(88.8)
19.99	10.18	9.81	9.04	0.491	320	16.0	35.4	32.6	106.8	92.2
10.00	5.135	4.865	4.58	0.486	163	16.3	35.6	33.5	108.8	94.0
5.00	2.592	2.408	2.30	0.482	81.5	16.3	35.4	33.8	110.7	95.6
2.00	1.054	0.946	0.918	0.473	32.6	16.3	35.5	34.5	112.2	96.9
1.00	0.532	0.468	0.458	0.468	16.2	16.2	35.4	34.6	113.3	97.8
0.00				0.462	0.0	16.4	35.5	35.5	115.8	100.0

A comparison of the values of γ_{KI_3} with those of γ_{KI} (Table III) shows that the degree of ionization of potassium tri-iodide is practically identical with that of KI up to a concentration of 0.1 normal. Each of the ratios $1000 (L - L')/(I_3^-)$ is therefore a separate determination of $(\Lambda_I - \Lambda_{I_3})$, the difference between the equivalent conductances of the tri-iodide ions. The average value of $\Lambda_I - \Lambda_{I_3}$ is 35.5, from which it follows that

$$\Lambda_{I_3} = 41.0 \text{ and } \Lambda_0 \text{ for } KI_3 = 115.8.$$

The limiting value (at zero concentration) of the ratio $\Delta\Lambda/r$ is equal to $\Lambda_I - \Lambda_{I_3}$, and the limiting values of $\Delta\Lambda$ and of r are therefore not independent. In the table $\Delta\Lambda$ is shown to increase slightly with increasing dilution, and the limiting value is probably as high as 16.4. It follows that, in solutions saturated with iodine, the ratio $r = (\Sigma I_3)/(\Sigma I + \Sigma I_3)$ tends toward the value $16.4/35.5 = 0.462$ as the concentration approaches zero.

From the values of this ratio in the different solutions it is seen that the proportion of tri-iodide in a solution saturated with iodine increases steadily with increasing concentration,[2] the whole change between 0.0

---

[1] An interpolated value.

[2] A comparison with the values of this ratio $(\Sigma I_3)/(\Sigma I + \Sigma I_3)$ determined by Noyes and Seidensticker (THIS JOURNAL, 21, 217 (1899); *Z. physik. Chem.*, 27, 359) shows that the agreement is fairly good at 0.1 normal, but that their values at smaller concentrations are always larger than ours and that the difference increases rapidly with increasing dilution. Since, as they point out, their values at the lowest concentrations are apparently affected by large errors, it seems not improbable that their values at higher concentrations are similarly affected, though of course to a smaller

and 0.1 normal being about 8 per cent. This effect is identical in direction with the very marked effect which has been observed in more concentrated solutions, where the ratio of total iodine dissolved in total potassium salt decreases rapidly with increasing salt concentration.

A Deviation from the Law of Mass Action.

This result may be expressed in another way: In potassium iodide solutions saturated with iodine, the ratio $(I^-)/(I_3^-)$, which according to the law of mass action should be constant, decreases from 1.16 to 0.99 when the potassium salt increases from 0.0 to 0.1 normal.

We have used the results of Laurie[1] to calculate at higher concentrations the apparent values of this ratio which are obtained when the same assumptions are made as at lower concentrations, *viz.*, that the solubility of I_2 as such is 0.00132 millimolal, that all the dissolved iodine in excess of this amount is present as tri-iodide, and that KI_3 is ionized to the same extent as KI. In order, however, to allow for the expansion of the solutions when iodine was dissolved in them, approximate corrections have been introduced by the method described above. The concentrations in the saturated iodine solution are thus referred to the volume of solution containing the same number of mols of potassium salt as were present in 1 liter of the original potassium iodide solution. The results, together with our own results at lower concentrations, are included in the following table. The table also contains the corresponding values of the equilibrium "constant" $K = (I^-)(I_2)/(I_3^-)$, obtained by multiplying the ratios $C_{I^-}/C_{I_3^-}$ by the solubility of I_2, 0.00132.

TABLE V.—VALUES OF $(I^-)/(I_3^-)$ AND $(I^-)(I_2)/(I_3^-)$ IN KI SOLUTIONS SATURATED WITH IODINE.

ΣK	1.000	0.850	0.700	0.500	0.344	...	..
ΣI_2 combined, mols per liter.	0.711	0.578	0.440	0.295	0.189	...	..
I_2 combined (mols)	0.742	0.598	0.452	0.300	0.191	..	..
In the volume (cc.)	1043	1035	1027	1018	1011	...	..
$C_{I^-}/C_{I_3^-}$	0.35	0.42	0.55(?)	0.67	0.80	...	..
$K \times 10^3 = 1.32\, C_{I^-}/C_{I_3^-}$	0.46	0.55	0.72	0.88	1.06	...	..

ΣK	0.100	0.020	0.010	0 005	0.002	0.001	0.0
$C_{I^-}/C_{I_3^-}$	0.99	1.04	1.06	1.08	1.11	1.14	1.16
$K \times 10^3 = 1.32\, C_{I^-}/C_{I_3^-}$	1.31	1.37	1.40	1.42	1.47	1.50	1.53

On plotting the values of $(I^-)/(I_3^-)$ against log (ΣK) it was found that a straight line was obtained from 0.001 to 0.1 normal ΣK, and that this line produced to normal concentration gave the value $(I^-)/$

---

percentage extent. As a possible source of error in these experiments, the presence of an organic impurity in the water may be mentioned; the reaction of this with iodine would produce an iodide, and the proportion of tri-iodide found would therefore be too great, especially in the dilute solutions.

[1] Laurie, *Z. physik. Chem.*, 67, 627 (1909).

$(I_3^-) = 0.92$ instead of the much lower value found (0.35). Thus the decrease of this ratio in concentrated solutions is much more rapid than was to have been expected from the results in dilute solutions.

Additional information with regard to this deviation from the law of mass action was obtained by comparing these values of the equilibrium function $K = (I^-)/(I_2)/(I_3^-)$ in saturated I_2 solutions with those obtained at other I_2 concentrations (Table I). On plotting K against the concentration of I_2 as determined from partition experiments, it was evident that in a dilute potassium iodide solution ($\Sigma K = N/16$) the values of K are practically constant and equal to 1.40; that in 0.1 and 0.2 normal solutions K decreases slightly with increasing I_2 concentration; and that this decrease is very pronounced in concentrated potassium iodide solutions. From the results for the most concentrated solutions (normal ΣK) the value of K at zero I_2 concentration was found by extrapolation to be 1.34×10^{-3}, which is almost as large as the values found in dilute potassium iodide solutions. Thus the deviations from the mass action law are very slight when the concentration of I_2 is small.

An obvious explanation of this decrease of K in the concentrated potassium iodide solution, which has frequently been offered, is that a polyiodide higher than KI_3 is formed, and that its concentration increases as I_2 is increased. But a difficulty is at once encountered when we consider the equilibrium in the saturated I_2 solution, *e. g.*, $I_5^- = I^- + 2I_2$. Here the ratio of (I_5^-) to (I^-) should be constant, and yet solid iodine separates when a concentrated solution is diluted. We are led to the result that if a polyiodide is present its concentration cannot be a measure of its "activity"[1] in the reaction. But if this second assumption is necessary even when a higher polyiodide is assumed to be present, then it seems worth while to determine if the assumption of a variation of the ratio of activity to concentration for tri-iodide or iodide is alone sufficient to explain the phenomenon—without the assumption of a higher polyiodide.

This concept of "activity" as introduced by Lewis is of great value in dealing with a problem involving a deviation from the law of mass action. For our purposes it is sufficient to recall that the following law is a thermodynamic consequence of the definition of activity. If the value of the activity (A) of each substance at equilibrium is substituted for its concentration in the mass-action expression, then the resulting activity function is a constant. Thus for the equilibrium, $I_3^- = I^- + I_2$, at constant temperature, $A_{I^-} \times A_{I_2}/A_{I_3^-} =$ constant. For our purposes we may, for the sake of convenience, place the activity (A) of each substance equal to the concentration (C) at infinite dilution.[2] As the concentration increases the activity will, in general, differ from the concentration, and the ratio of activity to concentration will also be altered when other substances are introduced into the solution. The problem of deviations from the law of mass action is thus resolved into the problem of determining how the ratio of activity to concentration varies for each substance under varying conditions. In the following we shall designate this ratio by the letter

---

[1] Lewis, *Proc. Am. Acad.*, 43, 259 (1907); *Z. physik. Chem.*, 61, 129 (1907).

[2] This is only justifiable when, as in the present instance, we are dealing with a

$$\rho = A/C.$$

We shall assume throughout that the concentration of any ion has the value derived from conductance measurements.

In the present example we may therefore conclude that at 25°, in solutions saturated with iodine,

$$A_{I^-}/A_{I_3^-} = C_{I^-}/C_{I_3^-} \text{ (for } K_{KI} = 0) = 1.16.$$

It is evident that the activity of I_2 as such is constant in all solutions in equilibrium with solid I_2, and may be considered equal to its solubility in pure water, since the concentration is very small, that ,is: $A_{I_2} = C_{I_2} = 0.00132$. The activity function,

$$K_A = A_{I^-} \times A_{I_2}/A_{I_3^-},$$

has therefore the value $1.16 \times 0.00132 = 0.00153$. This quantity, K_A, in virtue of the definition of activity, is, at any given temperature, constant under all circumstances. In the investigations of the equilibrium in solutions unsaturated with iodine (Table I) it is evident that the activity of I_2 in the aqueous phase, and not its concentration, was determined by the partition experiments.[1] The quantity K_1 (Table I), which is equal to K since γ' is now assumed equal to γ, therefore has the form

$$K = C_{I^-} \times A_{I_2}/C_{I_3^-}.$$

From the values of K, given in Tables I and V, we may calculate the values under different conditions of the expression

$$K_A/K = \rho_{I^-}/\rho_{I_3^-} = 0.00153/K.$$

Thus in 0.1 and 1.0 normal potassium iodide solutions the limiting values approached by the ratio $\rho_{I^-}/\rho_{I_3^-}$ as C_{I_2} approaches zero are $1.53/1.40 = 1.09$ and $1.53/1.34 = 1.14$, respectively; while in 0.0, 0.1 and 1.0 normal potassium iodide solutions saturated with iodine the values are 1.0, 1.17 and 3.34, respectively.

Thus if we can determine how one of the activity-concentration ratios,

---

single solvent at a constant temperature. In other cases it is best to adhere to the original definition of Lewis, according to which $A = C$ at infinite dilution only in the gaseous phase.

[1] This is exact only when the activity of iodine is proportional to its concentration in the organic solvent used in the partition experiments, which, however, is doubtless true, or nearly so, for CCl_4, $CHCl_3$, and CS_2, the solvents used.

as $A_{I^-}/C_{I^-} = \rho_{I^-}$, varies under different conditions we can at once calculate the corresponding values of the second ratio. As we shall see later, ρ_I^- is nearly constant, whence we conclude that $A_{I_3^-}/C_{I_3^-}$ decreases rapidly:

(1) in saturated I_2 solutions with increasing KI, and

(2) in a normal KI solution with increasing I_2.

Let us illustrate the significance of a variation in this ratio for a given substance. When the substance is at the same concentration in two different solvents, *M* and *N*, and has a smaller activity in *M*, then it will tend to escape from *N* to *M* (*e. g.*, through the gaseous phase if it is volatile). In such a case it is frequently stated that *M* is a "better solvent for the substance." Whenever the addition of any substance to a solution causes a decrease in the ratio of *A*/*C* for the original solute, the same idea may be applied by saying that the solution has become a better solvent for that solute.

In the present example we may thus state that a concentrated KI — I_2 solution is a better solvent for tri-iodide than is a pure potassium iodide solution or pure water. This phenomenon is doubtless connected with the mutual solubility of KI and I_2,[1] an idea which has been expressed by Parsons[2] in the phrase "solution in a dissolved solid."

The Composition of Concentrated Potassium Iodide Solutions Saturated with Iodine.

Important evidence relating to the presence of polyiodides higher than KI_3 in concentrated potassium iodide solutions saturated with iodine is furnished by the electromotive force determinations of Laurie.[3] The problem, however, cannot be completely solved without the knowledge, for some substance as I^-, of the variation of the activity concentration ratio in the saturated iodine solutions with increasing potassium iodide concentration. Accordingly, in the following detailed calculations the simple assumption referred to above has been made that $C_{I^-} = A_{I^-}$. Other assumptions are considered later and the complete results are summarized in Table VI.

In Laurie's measurements a half-cell containing 0.0005 mol I_2 dissolved in a potassium iodide solution was combined with another containing the same potassium iodide solution saturated with iodine. The diffusion potentials were eliminated by inserting between the half-cells a 10 times normal solution of ammonium nitrate.[4]

---

[1] The great solubility of KI in liquid iodine has been noted by Lewis and Wheeler, *Z. physik. Chem.*, 56, 179 (1906).

[2] Parsons, *J. Physic. Chem.*, 11, 669 (1907).

[3] Laurie, *Z. physik. Chem.*, 67, 627 (1909).

[4] Cumming's tests of this method, *Trans. Faraday Soc.*, 2, 213 (1906) depend upon the agreement between the measured e. m. f. (using 10 *N* NH_4NO_3), and the value calculated from the Nernst equation; but he used concentrated solutions, such as *N*

When the electrode reaction is considered to be

$$I^- + \oplus = {}^1/_2 I_2,$$

then the electromotive force (aside from the diffusion potential) is:

$$E = 0.0591 \ [\log (A_{I^-})_d/(A_{I^-})_s - {}^1/_2 \log (A_{I_2})_d/(A_{I_2})_s]$$

where the subscripts d and s refer to the dilute and saturated solutions, respectively.

By means of this equation the quantity which we wish to determine $(A_{I^-})_s$ may be calculated, since E was measured by Laurie and the other three activities may be derived as follows:

In the experiment with normal potassium iodide solutions,

$$E = 0.1252 \text{ volts.}^1$$

By our assumption,

$$(A_{I^-})_d = (C_{I^-})_d = 0.79 \times 0.9995 = 0.790,$$

where 0.79 is the degree of ionization of the potassium iodide and 0.9995 its concentration (the remaining K salt, 0.005, being present as triiodide).

The activity of iodine in any phase in equilibrium with solid I_2 has a constant value; as explained above

$$(A_{I_2})_s = 0.00132.$$

Finally $(A_{I_3^-})_d$ may be calculated from the equations

$$(A_{I_3^-})_d = (C_{I_3^-})_d/1.14 = 0.79 \times 0.0005/1.14 = 3.46 \times 10^{-4},$$

and

$$(A_{I_2})_d = K_A(A_{I_3^-})_d/(A_{I^-})_d = 0.00153 \times 3.46 \times 10^{-4}/0.790 = 6.70 \times 10^{-7}.$$

It is to be noted that the assumption is here made that the proportion of higher polyiodide such as KI_5 is negligible in this dilute I_2 solution, but this is evidently justifiable since we shall find that its concentration is small even in the saturated I_2 solution.

On substituting these values in the above electromotive force equation, it is found that $(A_{I^-})_s = 0.267$, which, according to our assumption, is equal to $(C_{I^-})_s$.[2] According to the view adopted early in the

---

HCl — 0.1 N HCl, in which it is very doubtful if the Nernst equation will give accurate results. Therefore the accuracy of the NH_4NO_3 method of eliminating potential differences is still unknown; but it is probably sufficiently accurate in the present instance for our purpose.

[1] In Laurie's article, page 632, the "NH_4NO_3 correction" of 0.0008 volt is a misprint for 0.0080.

[2] Laurie considered the electrode reaction $I^- + \oplus = \frac{1}{2}I_2$, and applied the Nernst formula, thus tacitly assuming that $A_{I^-} = C_{I^-}$. It is interesting to note that if he had adopted the equally possible electrode reaction $I_3^- + \oplus = {}^3/_2 I_2$ he would have obtained absolutely different results, since this corresponds to the assumption that $A_{I_3^-} = C_{I_3^-}$. Since Laurie adopted the first view his value for the concentration of I^- (0.264), is almost identical with ours (0.267). But he assumed that the degree of ionization depends upon the actual concentration of potassium iodide present, and his values for C_{KI} are therefore smaller than ours.

paper the degree of ionization of potassium iodide in this mixture depends on the total ion concentration and therefore is the same as in the pure potassium iodide solution. It follows that the total concentration of iodide, $C_{\Sigma I} = 0.267/0.79 = 0.338$, a value which is obviously independent of the degree of ionization originally assigned to the normal potassium iodide solution.

The total concentration of the potassium salt present in other forms than potassium iodide is therefore $1.000 - 0.338$ or 0.662, while the concentration of combined iodine is 0.742 mol I_2. This result evidently indicates that a small amount of a polyiodide higher than KI_3 is present. If we consider it to be only KI_5, then we have

$$C_{\Sigma I_5} = 0.080 \text{ and } C_{\Sigma I_3} = 0.582.$$

We thus reach a conclusion similar to that of Laurie, that a large part of the dissolved iodine in the normal potassium iodide solution saturated with iodine is present as tri-iodide. A similar treatment of the remaining measurements shows that the amount of higher polyiodide decreases as the potassium iodide concentration is decreased, and becomes negligible in the neighborhood of the 0.1 normal solution.

The activity of the tri-iodide ion in the normal potassium iodide solution saturated with I_2 is given by the equation,

$$(A_{I_3^-})_s = (A_{I^-})_s/1.16 = 0.230.$$

If the KI_3 is ionized to the same extent as KI, then the ratio of $A/C =$ for tri-iodide ion is: $0.230/0.79 \times 0.582 = 0.50$, which, of course, is considerably larger than the value (1/3.34), which we have previously calculated on the assumption that no higher polyiodide was present. Our previous calculations, however, will hold for concentrations of ΣK below 0.1 normal.

For the sake of comparison with these results a second series has been calculated from the electromotive force measurements in a similar way on the much less probable assumption that $C_{I_3^-} = A_{I_3^-}$. The two sets of results are presented in columns III and I in the following table. This table also contains, in the second column, the corresponding results when, according to the extrapolation from dilute solutions made early in the paper the ratio $C_{I^-}/C_{I_3^-}$ is assumed to be 0.92, and in the last column those obtained from the sole assumption that no polyiodide higher than KI_3 is present.

An inspection of this table shows that this complicated problem has been reduced to the determination of the variation, with increasing potassium iodide concentration, of the ratio of activity to concentration for a single substance, as iodide ion, in a saturated iodine solution. It is evident that, no matter what assumption is made, one or more of the substances involved will show marked deviations from the law of the ideal solution that activity and concentration are equal.

TABLE VI.—ACTIVITIES AND CONCENTRATIONS OF THE CONSTITUENTS OF THE NORMAL KI SOLUTION SATURATED WITH I_2.

	(I) Assuming $C_{I_3^-} = A_{I_3^-}$.	(II) Assuming $C_{I^-}/C_{I_3^-} = 0.92$	(III) Assuming $C_{I^-} = A_{I^-}$.	(IV) Assuming $C_{\Sigma I_5} = 0$.
A_{I^-}	0.305	...	0.267	...
$A_{I_3^-}$	0.262	...	0.230	...
$C_{\Sigma I}$	0.463	0.408	0.338	0.258
$C_{\Sigma I_3}$	0.332	0.443	0.582	0.742
$C_{\Sigma I_5}$	0.205	0.149	0.080	0.000
$\Sigma_I/\Sigma_{I_3} = C_{I^-}/C_{I_3^-}$	1.39	0.92	0.58	0.35
A_{I^-}/C_{I^-}	0.83	0.89	1.00	1.20
$A_{I_3^-}/C_{I_3^-}$	1.00	0.71	0.50	0.36

In the case of an aqueous solution of a single salt several examples are known in which the activity of a univalent ion increases somewhat less rapidly than its concentration (derived from conductance measurements), and there are at present no exceptions to this rule. This has recently been emphasized by Lewis and von Ende[1] in connection with their work upon the electromotive force of thallous-ion concentration cells. Another illustration is evidently furnished by Jahn's investigations of chloride-ion concentration cells[2] from which he concluded that the degrees of ionization ordinarily calculated from conductance measurements are too high. Some additional examples will be considered in later articles.

From the analogy with Jahn's experiments it is extremely probable that investigations of iodide-ion concentration cells free from iodine, using for example thallium-thallous-iodide electrodes, will yield similar results, and that therefore the activity of iodide-ion in pure potassium iodide solutions increases somewhat less rapidly than its concentration. If this applies in the present case in which the solutions are saturated with iodine, then the composition of the normal solution considered above will probably lie between the values given in the second and third columns of the table, and the solution will contain a greater proportion of higher polyiodide than calculated by Laurie. It is also interesting to note that the activity of tri-iodide ion increases much less rapidly than its concentration, and that this is even more striking when A_{I^-} is equal to or increases more rapidly than C_{I^-}.

But it is by no means certain that the relationship between A_{I^-} and C_{I^-} in potassium iodide solutions free from iodine will be the same as that in solutions saturated with iodine, and the two cases must be considered as two separate experimental problems.

The relation between A_{I^-} and C_{I^-} in dilute potassium iodide solutions saturated with iodine may be determined by combining the results of electromotive force measurements of concentration cells, using iodine electrodes, with the values of C_{I^-} determined in the present investigation. Unfortunately, the existing measurements of Crotogino,[1] in which each iodine electrode was measured against a calomel electrode, are probably not very accurate, and the corrections for the diffusion potential cannot be readily calculated. The results[1] show that A_{I^-} increases more rapidly than C_{I^-}, which is an indication that the composition of the normal potassium iodide solution saturated with iodine is intermediate between the values given in the last two columns of Table VI, and that the amount of higher polyiodide present is very small. This conclusion, however, can scarcely be accepted as correct without further experimental investigation.

---

[1] THIS JOURNAL, 32, 732 (1910).

[2] Jahn, *Z. physik. Chem.*, 33, 545 (1900).

While this evidence is somewhat conflicting, it would seem that the results given in column III of Table VI cannot be very far wrong. Thus, roughly speaking, the ratio of activity to concentration for iodide ion is independent of the concentration. The same ratio for tri-iodide ion diminishes rapidly with increasing concentration, and in all probability the higher polyiodide ions will be found to show even greater abnormalities in the same direction.

Summary.

In this investigation, conductance measurements at 25° have been made with potassium iodide solutions between 0.1 and 0.001 normal, and of the same solutions when saturated with solid iodine. The solubility of iodine in each solution has also been determined.

These results have led to the conclusions that the degree of ionization of KI_3 in dilute solutions is practically identical with that of KI up to a

---

[1] Cf. Sammet, *Z. physik. Chem.*, 53, 674–5 (1905). Crotogino's results, recalculated, are presented in the following table, the potential of the $N/16$ KI electrode being taken as zero. The last column contains the values of E calculated by means of the formula

$$E = 0.0591 \log C'_{I^-}/C''_{I^-},$$

i. e., on the assumption that $A_{I^-} = C_{I^-}$. The values of C_{I^-} are calculated from the data given in Table IV.

ELECTROMOTIVE FORCE MEASUREMENTS OF CROTOGINO.

ΣK.	C_{I^-}.	E measured.	E calc
$N/1024$	0.000509	—0.122	—0.102
$N/256$	0.001956	—0.081	—0.068
$N/64$	0.00744	—0.040	—0.034
$N/16$	0.0277	0.000	0.000
$N/4$	0.0980	0.0038	0.032

The large differences between E measured and E calculated are partly due to diffusion potentials, since the mobility of K^+ is greater than that of I_3^-. We have calculated approximately that 4 millivolts is the value of the diffusion potential between two solutions where there is a fourfold change in the concentration of ΣK; but, since the measurements were made against a calomel electrode, this value must be too high. It is therefore evident that E measured is always greater than E calculated, and that A_{I^-} increases somewhat more rapidly than C_{I^-}.

concentration of 0.1 normal; and that the conductances at 25° of iodide ion and tri-iodide ion are 76.5 and 41.0, respectively, that of potassium-ion being assumed equal to 74.8.

Burgess and Chapman, by means of transference experiments, have made an independent determination of Λ_{I_3} and found a value only slightly greater than ours, namely 42.5. We have therefore adopted an intermediate value, 41.5, as the most probable value of Λ_{I_3}.

It has also been found that in potassium iodide solutions saturated with iodine the ratio $C_{I^-}/C_{I_3^-}$, which according to the law of mass action should be a constant, decreases from 1.16 to 0.99 between 0.0 and 0.1 normal; thus showing that an effect due to the presence of potassium iodide, which has been known to exist in more concentrated solutions, is not negligible even in these very dilute solutions.

Finally we have attempted to determine the composition of concentrated solutions of potassium iodide saturated with iodine, and have illustrated the usefulness of the concept of "activity," as defined by Lewis, in dealing with deviations from the law of mass action. An examination of the existing solubility and electromotive force data has shown that the problem may be solved if the relation between the activity and concentration of iodide ion in solutions saturated with iodine is known. By concentration of an ion is understood the value ordinarily calculated from conductance measurements. Although the somewhat conflicting nature of the evidence prevents an exact solution of the problem, the conclusion is reached that the ratio of activity to concentration for iodide ion is nearly independent of the concentration, that the same ratio for tri-iodide ion decreases rapidly in the concentrated solutions, and that probably higher polyiodide ion show this abnormality in an even higher degree. In a normal potassium iodide solution saturated with iodine, the concentration of KI_5 is calculated to be about 0.08 molal, if this is the only higher polyiodide present.

BOSTON, May, 1910.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 53.]

THE HYDROLYSIS OF IODINE AND OF BROMINE.

BY W. C. BRAY.

Received June 13, 1910.

I. The Hydrolysis of Iodine.

During the investigation described in the preceding paper, we were confronted with the problem of how to account for the conductance of aqueous iodine solutions. From calculations based on Sammet's[1] determinations of the equilibrium constants, we were led to conclude that both of the following reactions must be considered:

---

[1] *Z. physik. Chem.*, 53, 687 (1905).

$$(1)\quad I_2 + H_2O = H^+ + I^- + HIO, \text{ and}$$

$$(2)\quad 3I_2 + 3H_2O = 6H^+ + 5I^- + IO_3^-;$$

and we could predict that the conductance would rise very rapidly at first (reaction (1)), and continue to rise slowly (reaction (2)) to a much higher value than we had found in our preliminary experiments. This prediction has been completely verified by the results of the conductance and solubility measurements described below.

The experimental methods employed were the same as in the experiments described in the preceding article. All measurements were made at 25°. In the final conductance experiments three different portions of powdered iodine were used; these were rotated with frequently renewed portions of water over a period of about three weeks to ensure the removal of all soluble impurities. The conductance then showed a constant value when measured after two hours' rotation. The measurements were made in a low resistance cell with smooth electrodes. The conductance of the water used varied between 0.4 and 0.9×10^{-6}; it was determined in each case and subtracted from the measured conductance. Some experiments with water alone showed that under the regular experimental conditions its conductance changed very little; in 16 hours from 0.89 to 0.94×10^{-6}; in 41 hours 0.58×10^{-6}, unchanged; in 54 days from 0.44 to 1.5×10^{-6}.

The conductance measurements for aqueous solutions are given in Table I:

TABLE I.—SPECIFIC CONDUCTANCE × 10^6 OF IODINE IN AQUEOUS SOLUTIONS.

Hours rotation.	1/4.	2.	4.	8.	15.	16.	18.	21.	40.	(54×24.)
Portion I	3.8	...	..	...	...	...	4.9	4.7	...	19.1
Portion II	...	4.0	4.3	4.7	4.9	4.8	...	...	...	63.9(?)
Portion III	3.8	3.9	4.0	4.0	4.5	4.6	...	...	5.4	..

These results show that the specific conductance of aqueous iodine solutions rises rapidly to 4.0×10^{-6}, and continues to rise very slowly for a long period of time. The results obtained with Portion II are uniformly high, which is due to the fact that the stopper of the bottle did not fit properly; the introduction of an organic impurity and the resulting formation of an iodide would explain the very high result (63.9).

In order to determine the effect of the presence of hydrogen ion the preceding experiments were repeated with approximately 0.001 *N* HCl and HNO_3. In each case the iodine was first washed with the acid and then rotated over night with it before making measurements, in order to eliminate changes due to adsorption. The first two experiments in Table II were performed with the iodine of Portion I in a cell with platinized electrodes which had been heated;[1] the remaining two were preliminary experiments made at an earlier date by Mr. Mackay in a cell with platinized platinum electrodes. The conductance of the acid was measured at the time the acid was added to the iodine.[2]

TABLE II.—SPECIFIC CONDUCTANCE × 10^6 OF IODINE IN 0.001 *N* ACID SOLUTIONS.

Acid used. Hours rotation	HCl. 3.	HCl. 15.	HCl. 42.	HNO_3. 42.
Acid + iodine	420.0	420.2	419.4	417.4
Acid alone	418.8	419.3	418.1	416.3
Difference	1.2	0.9	1.3	1.1

These values for the conductance of iodine are the differences between two large numbers and are therefore much less accurate than the determinations in aqueous solutions. But these results, obtained under widely different circumstances, make it almost certain that the specific conductance of iodine in acid solution is about 1 × 10^{-6}, which is much smaller than the value obtained in pure water.

These experiments were also repeated with 0.001 *N* NaCl solution, using the iodine of Portion III, Table I, in order to determine if the decreased conductance of iodine in the acid solution was due merely to the presence of an ionized substance:

TABLE III.—SPECIFIC CONDUCTANCE × 10^6 OF IODINE IN 0.001 *N* NaCl SOLUTION.

Hours rotation.	1/2.	3.	7.	14.	(55×24.)
NaCl + iodine	130.2	130.4	130.4	131.0	137.3
NaCl alone	127.1	127.1	127.1	127.0	127.0
Difference	3.1	3.3	3.3	4.0	10.3

The conductance of iodine in dilute sodium chloride is thus seen to increase in a manner very similar to that observed in water solutions, though the values obtained are somewhat smaller. The specific conductance (× 10^6) rises rapidly to 3.3 (in water 4.0) and remains nearly constant for several hours; in 14 hours it reaches the value 4.0 (in water 4.6); and in 54 days increases to 10.3 (in water 19.1).

The probable explanation of these results is that the initial value of the conductance of aqueous iodine solutions is mainly due to the rapidly occurring hydrolysis:

$$I_2 + H_2O = H^+ + I^- + HIO,$$

and that this hydrolysis is driven back almost completely in acid solutions.[3]

---

[1] Whetham and Griffiths, *Phil. Trans.*, 194A, 330 (1900).

[2] In two blank experiments in which the hydrochloric acid alone was rotated in the thermostat for two days the conductance remained unchanged.

[3] It is possible that the conductance of iodine in acid solution, 1 × 10^{-6}, is due to the presence of the ions $I^- + I^+$ (cf. W. A. Noyes, THIS JOURNAL, 23, 463 (1901); Stieglitz, *Ibid.*, 23, 797 (1901); Walden, *Z. physik. Chem.*, 43, 415 (1903)). If this is true, then in KI solutions the concentration of I^+ would be reduced to a very small value.

As a check on this result, the relative solubilities of iodine in water and dilute hydrochloric acid have been determined, and also the change of them with the time. The saturated solution was forced into a 100 cc. pipette through an asbestos filter connected with it by a ground-glass joint; the 100 cc. were run into a potassium iodide solution containing sulphuric acid, and the titration was made with freshly prepared (approximately) $N/200$ thiosulphate. The thiosulphate solutions were not accurately standardized, since the measurements desired were only comparative. The value adopted for the total solubility of iodine at 25° was that of Hartley and Campbell,[1] 0.001337 mol I_2 per 1000 grams water, or 0.001333 mol per liter; the solubility, after two hours' rotation, being assumed to have this value. After each experiment extending over a long period of time, the iodine was washed with water and its solubility again determined by rotating it two hours with fresh water. The iodine used in the experiments with 0.001 N HCl was Portion III; in the aqueous solutions Portions I and II. In these experiments only the first 100 cc. portion from each 250 cc. bottle was used, since the second portion, when taken, gave somewhat lower results.

TABLE IV.—RELATIVE SOLUBILITY OF IODINE IN WATER AND IN HYDROCHLORIC ACID SOLUTIONS.

Solvent.	Water.		0.001 N HCl.		0.001 N NaCl.
Time.	Iodine.	Iodate.	Iodine.	Iodate.	Iodate.
1.5 hours...........	2.664	..	...	..	...
2 hours...........	2.666[2]	0.002 or less	2.639	..	...
2 hours...........	..	..	2.639	..	...
3 hours...........	2.666	..	..	..	...
16 hours...........	2.668	..	2.653	..	...
41 hours...........	2.666	0.010 or less	2.665	0.010 or less	...
48 hours...........	2.665	..	...	..	...
27 days............	2.80	..	2.72	0.017 or less	...
27 days............	2.83	0.017	...	..	...
54 days............	..	0.027	...	..	0.025

The iodate concentration was also determined approximately by adding 100 cc. of the saturated solution to a potassium iodide solution containing sodium hydrogen carbonate and an excess of carbonic acid, decolorizing with thiosulphate, adding excess of sulphuric acid, and titrating after 3–5 minutes the iodine now liberated by the action of HIO_3

---

[1] *J. Chem. Soc. Trans.*, 93, 741 (1908). These authors made an extended series of measurements at different temperatures and used carefully purified iodine and conductivity water. Other determinations (in mols per liter) are, Jakowkin, 0.001337; Noyes and Seidensticker, 0.001342; Sammet, 0.001341.

[2] Value derived from several concordant experiments.

on HI.[1] By determining roughly the rate at which iodine is subsequently liberated by the action of oxygen on hydriodic acid, the very small error due to this reaction was eliminated. The iodate was also determined in a single experiment in which the solvent was 0.001 *N* NaCl (in which iodine, Portion III, was used). The results are given in Table IV, in milliequivalents (of $^1/_2I_2$ and $^1/_6HIO_3$) per liter.

The solubility of iodine in the acid solution is (after two hours) just one per cent. less than in water, which is at any rate qualitatively in agreement with the conductance results. The solubility increased slightly in two days in the acid, but remained practically constant in the aqueous solution; and later increased steadily in both cases.[2]

If we assume that the initial solubility in the acid solution is a measure of the true solubility of iodine as I_2, then this value is 1.320 millimols per liter. From the 41-hour experiment, after correcting for the iodate and the tri-iodide due to the iodide formed in the reaction, the value 1.320 is again obtained. The most probable source of error is the presence of iodide (and consequently tri-iodide), and the results are therefore more likely to be too high than too low.

Another method of calculating the true solubility is to correct the value found in pure water by means of the conductance data, Table I. Assuming that the conductances, 4.0, 4.6, and 5.4, after 2 16, and 41 hours, respectively, are due solely to the acid (mainly HI) formed by the reactions (1) and (2), then the ion concentrations obtained by dividing them by $\Lambda_H + \Lambda_I = 425$ are approximately 0.0094, 0.0108 and 0.0127 millimol per liter. The corresponding iodine concentrations (in equivalents), which are to be subtracted from the solubilities are approximately three times these values; since for each equivalent of H^+ there are two oxidation equivalents of HIO (or IO_3^-) and roughly one oxidation equivalent (= 0.5 mol) of I_3^- (since about one-half of the iodide ion originally formed is converted into tri-iodide ion). The true solubilities after 2, 16 and 41 hours are therefore 1.320, 1.318 and 1.314 millimols I_2 respectively. These results may be too low if the conductance is not wholly due to the acid formed in the reactions (1) and (2).

The agreement between these two independent methods confirms the correctness of both, and the value 1.32 millimols I_2 per liter was therefore chosen as the true solubility at 25° of iodine as such.

[1] Bray, *Z. physik. Chem.*, 54, 470 (1905). The amount of dilute thiosulphate required in the first stage of the titration was always considerably less than the theoretical amount, but increased when the concentration of potassium iodide present increased. This phenomenon is probably due to direct oxidation of the thiosulphate to sulphate (cf. *Ibid.*, 472).

[2] The unexpectedly high values for the 27-day experiments may be due to an experimental error, since all depend on a single (comparative) determination of the solubility of iodine after two hours; but are more probably due to the entrance of some organic matter through the stoppers.

It is now possible to calculate the equilibrium constant of the hydrolysis: $I_2 + H_2O = H^+ + I^- + HIO$, from the above given value of the H^+ concentration. Since it seems probable that the initial conductance 4.0×10^{-6} of an aqueous solution is a measure of the hydriodic acid formed in this reaction, $(H^+) = (I^-) = (HIO) = 0.94 \times 10^{-6}$ mols per liter, and the equilibrium constant

$$(H^+)(I^-)(HIO)/(I_2) = 0.6 \times 10^{-12}.$$

This value is much smaller than the limiting values, 10^{-8} to 10^{-10} estimated by Sammet; but he considered his results to be of very little value and gave no details of his measurements.

It is interesting to calculate the maximum conductance which should be finally attained by the saturated aqueous solution as a result of reaction (2) from Sammet's (accurate) value of its equilibrium constant: $(H^+)^6(I^-)^5(IO_3^-)/(I_2)^3 = 2.8 \times 10^{-47}$. The concentrations of the other substances are calculated from the known concentration of the iodine to be: $(H^+) = 3.16 \times 10^{-5}$, $(I^-) = 2.63 \times 10^{-5}$, and $(IO_3^-) = 0.53 \times 10^{-5}$, and the corresponding specific conductance is calculated to be 13×10^{-6}. This value is somewhat larger than that obtained in the sodium chloride solution, 10.3×10^{-6}, and somewhat smaller than the value in aqueous solution, 19.1×10^{-6}.

II. The Hydrolysis of Bromine.

It is well known from the comprehensive investigation of Jakowkin[1] that dilute solutions of chlorine are hydrolyzed to a very considerable extent. The hydrolysis constant at 25° is

$$(H^+)(Cl^-)(HClO)/(Cl_2) = 4.48 \times 10^{-4}.$$

Since bromine occupies an intermediate position between chlorine and iodine in so many instances, it is almost certain that bromine solutions will also exhibit hydrolysis. This hydrolysis is mentioned in a recent article by Jakowkin,[2] but no experimental data are given. In the following some preliminary measurements are described:

A large portion of liquid bromine was placed in a 250 cc. bottle and shaken successively with eight portions of fresh water. Conductance measurements were made, and the correction for the specific conductance of water applied, as in the preceding experiments. Portions of each solution were also removed in a small pipette designed to prevent an error due to evaporation; and were added to a concentrated solution of potassium iodide containing sulphuric acid; the liberated iodine was titrated with thiosulphate. The results are presented in the following table. In experiments 3(*b*) and 7(*b*) the water was not renewed. In the final experiment, the solution was probably not saturated, since the amount of bromine left was very small.

---

[1] Jakowkin, *Z. physik. Chem.*, 29, 613 (1899).

[2] Jakowkin, *Ibid.*, 70, 188 (1910).

TABLE V.—CONCENTRATION AND CONDUCTANCE OF SATURATED BROMINE SOLUTIONS

No.	Time (hours)	Equiv. conc.	Spec. cond. × 10^6.
2	70	0.506	7440
3*a*	1	0.465	4160
b	20	0.466	4160
4	2	0.440	2210
5	1	0.424	907
6	1	0.424	734
7*a*	1	0.411	726
b	6	0.425	805
8	2	0.411	728

The concentration decreases slightly, and the conductance greatly in the first five experiments, probably owing to the gradual removal of some impurity, such as hydrobromic acid or potassium bromide. The bromine appears, from the approximate constancy of the two series of results, to have been nearly pure in the last four experiments; and the following values are probably not greatly in error: solubility, 0.21 mol Br_2 per liter;[1] specific conductance, 727×10^{-6} reciprocal ohms.

If we assume that the conductance is solely due to the hydrobromic acid formed by the hydrolysis, $Br_2 + H_2O = H^+ + Br^- + HBrO$, then the concentration calculated for $(H^+) = (Br^-) = (HBrO)$ is 0.0017. This corresponds to 0.8 per cent. hydrolysis, and the calculated equilibrium constant is:

$$(H^+)(Br^-)(HBrO)/(Br_2) = 2.4 \times 10^{-8}.$$

This value differs very little from the geometric mean, 1.7×10^{-8}, of the hydrolysis constants of chlorine and iodine.

Summary.

From conductance and solubility measurements of iodine and of bromine in water, the hydrolysis constants $(H^+)(I^-)(HIO)/(I_2)$ and $(H^+)(Br^-)(HBrO)/(Br_2)$ are found to be 0.6×10^{-12} and 2.4×10^{-8}, respectively.

BOSTON, March, 1910.

THE THERMAL DISSOCIATION OF CALCIUM CARBONATE.

BY JOHN JOHNSTON.

Received June 16, 1910.

Measurements of the dissociation pressures of calcium carbonate have been made through a range of temperatures by Debray,[2] LeChatelier,[3]

---

[1] This value agrees well with that determined by Winkler (Seidell, solubilities, page 67) 3.36 g. per 100 g. soln., or approximately 0.206 mol per liter.

[2] *Compt. rend.*, 64, 603 (1867).

[3] *Id.*, 102, 1243 (1886).

Brill,[1] Pott[2] and Zavriev.[3] Quite recently, E. H. Riesenfeld[4] has discussed the data of each of these authors. He concludes that, owing to errors in the measurement of pressure or of temperature, or of both, the data of the first three authors are altogether untrustworthy, and sets up an involved empirical formula to express the mean results of Zavriev and Pott. Pott made four series of measurements over the temperature range 600–900°; these, however, are by no means so concordant as might be wished, *e. g.*, for 892° he found pressures which varied from 593 mm. to 776 mm. Still, a curve drawn through the midst of his points coincides approximately with that which represents the results of Zavriev, which are relatively few in number but more concordant among themselves.

From the results of either author it follows that the dissociation point (*i. e.*, the temperature at which the pressure of carbon dioxide is one atmosphere) is close to 910°. This value was confirmed by special experiments made by Riesenfeld, who determined anew the temperature at which a loss of weight occurred when the carbonate was heated in an atmosphere of pure carbon dioxide. He showed, moreover, that the possibility of formation of solid solutions of calcium oxide in the carbonate and *vice versa* is practically excluded, while it was shown by Zavriev that no basic carbonate exists.

It has therefore now been definitely proved that the dissociation of calcium carbonate proceeds according to the scheme $CaCO_3 \rightleftarrows CaO + CO_2$, and to that scheme solely. The discrepancies in the results are thus to be attributed entirely either to errors in the measurement of the temperature of the substance, or to errors in the pressure, due either to the fact that equilibrium conditions had not been attained or to the presence of water vapor or of some other impurity capable of developing a pressure.[5]

The apparatus used by both Pott and Zavriev consisted essentially of a long porcelain tube closed at one end, connected to a manometer at the other. In this tube were placed quantities of substance weighing from 2–5 grams, and the thermoelement was embedded in the charge in such a way that the junction was in the hottest part of the furnace. Now Zavriev observed directly differences of more than 50° in the temperature at various points of somewhat larger charges contained in a boat 5 cm. in length; so it is not unreasonable to suppose that the temperature variations throughout the charge were still considerable in the actual measurements. This difficulty has been encountered in all accurate high temperature work, but its importance, and the magnitude of the error introduced thereby, have not yet been generally appreciated.[1] For accurate work it is of the highest importance that the temperature of the charge be as uniform as possible; for otherwise, since the carbon dioxide is in equilibrium with that calcium oxide which is at the *lowest* temperature, one cannot determihe with any certainty the appropriate temperature corresponding to the pressure observed. In the author's experiments,[2] this difficulty was obviated by using charges of only about 0.1 gram, the total vapor space being not more than 5 cc.; this possesses the additional advantage that a transfer of a very small amount of carbon dioxide from the solid to the vapor phase suffices to bring the system into equilibrium, and consequently equilibrium conditions are established comparatively rapidly.

---

[1] *Z. anorg. Chem.*, 45, 275 (1905).

[2] Dissertation, Freiburg in B., 1905.

[3] *Compt. rend.*, 145, 428 (1907); *J. chim. phys.*, 7, 31 (1909).

[4] *J. chim. phys.*, 7, 561 (1909).

[5] Cf. J. Johnston, *Z. physik. Chem.*, 62, 336 (1908); H. Schottky, *Idem.*, 64, 432 (1908).

The apparatus used was a slight modification of an apparatus previously described by the author.[3] The substance was contained in a platinum tube 6 cm. in length, 6 mm. in external and 5 mm. in internal diameter, which was sealed directly on to a glass tube and thereby, through an adjustable mercury trap, connected to a mercury manometer, on which the pressures were read directly with the aid of a fine mirror scale divided in millimeters. After complete evacuation of the apparatus, the platinum tube was heated gently for some time in order to expel any water or other volatile impurity; by manipulation of the stopcocks the mercury was raised in the trap, thereby delimiting the vapor space. The platinum tube was enclosed almost entirely in a small vertical resistance furnace, and was well packed with asbestos at the mouth of the furnace. The temperature was in general increased step by step; in a few cases it was dropped some degrees with a corresponding drop in the pressure. In all cases the reading was taken only when at constant temperature the pressure had attained a constant value; at low pressures, this required an interval of some hours, but at the higher pressures half an hour usually sufficed.

The temperature of the charge was measured by means of a thermoelement the junction of which was welded on to the outside closed end of the platinum tube; elsewhere the thermoelement wires were insulated by small Marquardt tubes. The element used had previously been carefully calibrated at the melting points of zinc, silver and copper (418°,

---

[1] Cf. Day and Sosman, *Am. J. Sci.*, 29, 99, 102 (1910); W. P. White, *Idem.*, 28, 335 (1909).

[2] To avoid possible misunderstanding, it may be stated that the measurements were completed in April, 1909; that at that time I had seen only the preliminary paper of Zavriev (*Compt. rend.*, 145, 428 (1907)), and was entirely unacquainted with the work of Pott; further, that Table 1 is a complete record of the measurements which I have made.

[3] *Z. physik. Chem.*, 62, 333, 335 (1908).

960°, and 1083° respectively), the electromotive forces being measured by the usual arrangement of potentiometer and galvanometer. After being welded on the element was compared several times with a previously calibrated standard element the junction of which was immersed in calcium carbonate inside the platinum tube, the other conditions being precisely those of the actual pressure measurement. By this means it was shown that the maximum variation in the temperature of the charge did not exceed 2° and that the difference between the temperature registered by the element welded outside and that of the standard element inside the tube was 2.5° at 400° and 5° at 900°,[1] the variation being practically linear. All the temperatures given have been corrected for this difference, and it is considered that they are certainly correct to within ±2°. Four series of observations were made; in two series, pure precipitated calcium carbonate alone was used, some carbon dioxide being driven off by the initial heating after evacuation; in the other two series, the substance taken was a mixture of the pure carbonate with pure freshly ignited oxide. All the observations are brought together and arranged in Table 1; *p* is the pressure in millimeters of mercury, *t* and T the centigrade and the absolute temperatures respectively. These points are all plotted on Fig. 1, from which it is evident that they all lie close to the graph of equation VI*a*. The derivation of this equation will now be given.

TABLE 1.—ACTUAL EXPERIMENTAL RESULTS.

t	T.	*p*. in mm.	*t*.	T.	*p* in mm.
587	860	1.0	749	1022	72
605	878	2.3	777	1050	105
631	904	4.0	786	1059	134
			788	1061	138
671	944	13.5	795	1068	150
673	946	14.5	800	1073	183
680	953	15.8	819	1092	235
682	955	16.7	830	1103	255
691	964	19.0	840	1112	311
701	974	23.0	842	1115	335
703	976	25.5	852	1125	381
711	984	32.7	857	1130	420
			871	1144	537
727	1000	44	876	1149	557
736	1009	54	881	1154	603
743	1016	60	883	1156	629
748	1021	70	891	1164	684
			894	1167	716

---

[1] It was found that the absolute magnitude of these temperature differences varied within 1° or 2° with the depth of immersion of the platinum tube in the furnace and with the efficiency of the packing at the mouth of the furnace; this variation of the differences could, however, be rendered inappreciable by reproducing always the same conditions.

In a previous paper[1] it was shown that for a number of heterogeneous equilibria similar to that under consideration, the dissociation pressure is connected with the heat of reaction[2] ΔH by the equation

$$\log P = \frac{\Delta H}{4.576T} - \frac{I'}{4.576} \qquad (I)$$

I' being the so-called thermodynamically indeterminate constant; and that this relation holds within the limits of accuracy of our present knowledge of ΔH and of the other thermochemical quantities involved. The above simple relation is derived by neglecting all the higher terms; this is equivalent to the assumption that ΔH is independent of the temperature.

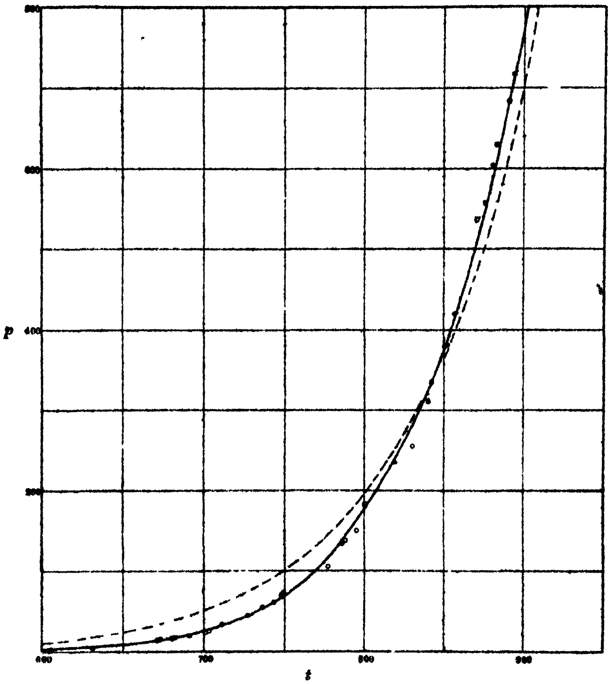


Fig. 1.—Experimental results on the dissociation pressure of $CaCO_3$. The full line is the graph of equation VI*a*; the broken line that of Riesenfeld's equation.

In the present case, our knowledge of the thermal quantities, though by no means satisfactory, is such that it is advisable to insert terms which shall represent the change of ΔH with the temperature. Consequently, we write $\frac{d(\Delta H)}{dT} = \Delta C_p$ and assume $\frac{d(\Delta C_p)}{dT} = \alpha$ where α is a constant; ΔC_p is the change in heat capacity of the system when the reaction $CaCO_3 = CaO + CO_2$ takes place. Hence, by integrating, we obtain

---

[1] THIS JOURNAL, 30, 1357 (1908); *Z. physik. Chem.*, 65, 737 (1909).

[2] ΔH is the amount of heat *absorbed*, as ordinarily measured calorimetrically, when the reaction $RCO_3 = RO + CO_2$ takes place. In the former paper, the pressure was expressed throughout in atmospheres; in the present paper, p is expressed always in millimeters mercury; this is more convenient, and causes only a numerical difference in the value of I. It may be noted that $4.576 \log P = R \ln P$ where ln is the natural log, and R the gas constant.

$$\Delta H = \Delta H_0 + \Delta C_{p0}\, T + \tfrac{1}{2}\, \alpha T^2 \qquad \text{(II)}$$

and therefore equation (I) becomes[1]

$$-RT \ln p = \Delta H_0 - \Delta C_{p0} T \ln T - \tfrac{1}{2}\, \alpha T^2 + I\, T \qquad \text{(III)}$$

In order to derive numerical values of the coefficients in equation (III) from the thermal data available, it is necessary to proceed in the following somewhat roundabout manner: The mean of the concordant values for the heat of reaction obtained by Thomsen and by de Forcrand is 42900 cal.; *i. e.*, $\Delta H = 42900$ when $T = 300°$. Now, by making a least square solution for all the experimental data comprised between $T = 1000°$ and $T = 1167°$ on the assumption that the equation $\log p = a/T + b$ holds (*i. e.*, on the assumption that within the above temperature range ΔH is fairly constant), we obtain the equation

$$\log p = -8419/T + 10.071 \qquad \text{(Ia)}$$

Hence at the mean temperature, say $T = 1100$, we have, by comparison with equation (I),

$$\Delta H = 8419 \times 4.576 = 38500 \text{ cal.}$$

By substitution of these pairs of values in equation (II) and elimination of ΔH_0, the equation

$$5.5 = -\Delta C_{p0} - 700\, \alpha \qquad \text{(IV)}$$

results; this can be solved by combining it with some recent results on the specific heats of calcium carbonate and oxide. Lindemann,[2] namely, found that the specific heat, at the ordinary temperature, of $CaCO_3$ was 0.2027; and that of CaO was 0.1821. Hence, the values of C_p (the molecular heat capacity) are 20.3 and 10.2 respectively. When $T = 300°$, C_p for CO_2, as deduced from the work of Holborn and Henning, is 9.0; hence

$$\Delta C_p = 9.0 + 10.2 - 20.3 = -1.1 \text{ when } T = 300.$$

This statement is equivalent to the equation

$$-1.1 = \Delta C_{p0} + 300\, \alpha \qquad \text{(V)}$$

from which, by combination with (IV), we obtain

$$\alpha = -0.011$$

$$\Delta C_{p0} = 2.2$$

and hence from II, $\Delta H_0 = 42700$.

---

[1] Cf. Haber, "Thermodynamics of Technical Gas Reactions," pp. 26, etc.; Johnston, *Loc. cit.*, p. 1358.

[2] Nernst, Koref, and Lindemann, *Sitzungsber. Akad. Wiss., Berlin*, 1910, 247.

Inserting these values, equation III becomes

$$-RT \ln p = 42700 - 2.2\ T \ln T + 0.0055\ T^2 + I\ T$$

which may be written in a form more convenient for calculation,

$$\log p = -9340/T + 1.1 \log T - 0.0012\ T - I''. \qquad \text{(VI)}$$

When the corresponding values of p and T are substituted in equation (VI), concordant values of I'' are obtained, the mean of which is —8.882. Finally, therefore, as the equation which represents p (expressed in mm. mercury) as a function of T (the absolute temperature) we have

$$\log p = -9340/T + 1.1 \log T - 0.0012\ T + 8.882. \qquad \text{(VI}a\text{)}$$

This equation reproduces the observations over the whole range within the probable error of experiment;[1] and since its form is theoretically the most satisfactory, consistent with present knowledge, it may be used with some confidence for extrapolation. By means of equation VI*a* the equilibrium pressures have been calculated for a number of temperatures (centigrade); the results are presented in Table II. The dissociation point is 898°.

These results are considered to be better than any of the existing data on the subject because of the superior accuracy with which the temperature of the dissociating substance was determined. For the sake of comparison, however, results interpolated graphically from the experimental data of Zavriev and of Pott are included in Table II.

TABLE II.—EQUILIBRIUM PRESSURES (IN MM.) FOR $CaCO_3$ AT ROUND TEMPERATURES.

t.	Calc. by equation VI*a*.	Interpolated from the data of Zavriev.	Pott.
500	0.11	...	...
550	0.57	...	...
600	2.35	..	...
650	8.2	...	...
700	25.3	43	53
750	68	95	101
800	168	197	195
850	373	381	350
900	773	697	667
950	1490	...	...
1000	2710	...	...

From the data of these authors, Riesenfeld deduced the mean values at five temperatures—700°, 750°, 800°, 850° and 900°;[2] and on the basis of these results, with the aid of the Nernst formula for heterogeneous equilibria, arrived at the equation[3]

---

[1] Equation I*a* fits the data from T = 1000 to T = 1167 almost as well as equation VI*a*; but, on account of the fact that ΔH actually does vary with the temperature, it is not satisfactory as an extrapolation formula.

[2] The values are close to the arithmetic means of columns 2 and 3, Table II.

[3] P is in atmospheres. It may be noted that the coefficient of the first term on

$$\log P = -9300/T + 1.75 \log T + 0.011{,}916\ T - 0.000{,}020{,}323\ T^2 + 0.000{,}000{,}008{,}2446\ T^3 + 3.2.$$

The graph of this equation over the experimental range is drawn as a broken line in Fig. 1, which shows that from about 800–900° the results from both equations are not very different. It is otherwise at other temperatures, and the discrepancy becomes especially noticeable at higher temperatures; at 1500°, Riesenfeld's equation leads to a value of 6,790,000 atmospheres, whereas equation VI*a* gives 151 atmospheres. In order to bring out the difference between the two formulas and the consequent uncertainty of extrapolation, Fig. 2 has been constructed by drawing the graphs of both equations for a range of temperature extending from 400–1500° C. This was accomplished by plotting the values of log *p* (in mm.) against those of $10^6/T$;[1] that part of either curve

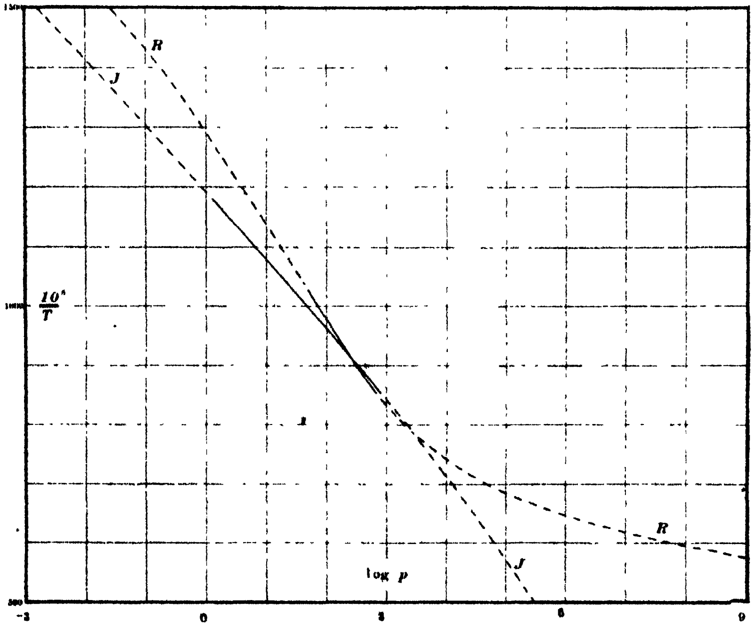


Fig. 2.—Graphs of Riesenfeld's equation (RR) and of equation VI*a* (JJ): the portions extrapolated are represented by broken lines.

---

the right-hand side is derived from the heat of reaction at room temperature, and is the only coefficient to which a direct physical interpretation can be given; that of the second term and the constant are taken from Nernst; the other three coefficients were chosen so as to fit the pressure data.

[1] Plotting with these coördinates possesses the advantages: that the graph of equations such as VI is nearly a straight line, and is absolutely a straight line so long as ΔH is independent of T; that the value of ΔH at any point can be readily derived from the slope of the curve at that point.

based on direct experiment is drawn full, while the extrapolated portions are represented by broken lines. Comment is unnecessary.

Summary.

In preceding measurements of the equilibrium pressure of the reaction $CaCO_3 \rightleftarrows CaO + CO_2$, the errors have been due mainly to a lack of definiteness in the temperature of the reacting system; in the author's experiments this difficulty has been obviated by the use of a very small quantity (0.1 gram) of material, by which means the extreme temperature variation throughout the charge did not exceed 2°. This necessitated the use of a form of apparatus in which the vapor space was always small; this, and the mode of measuring the temperature accurately, are described in the paper. It is considered that the uncertainty in the temperature is not greater than ±2°.

The results of four separate series of measurements can be well reproduced by the equation

$$\log p = \frac{-9340}{T} + 1.1 \log T - 0.0012\,T + 8.882$$

where p is the equilibrium pressure (expressed in millimeters of mercury) at the absolute temperature T. The pressure reaches one atmosphere at 898° C. Two of the numerical coefficients of the above equation are derived from the heat of reaction and the heat capacities of the components; the form of the equation is consistent with our present theoretical knowledge; consequently, in spite of the somewhat unsatisfactory character of the thermal data, the equation may be used with some confidence for extrapolation. The above equation represents the experimental results much better than the formula proposed by Riesenfeld, and derived from the approximation formula of Nernst; values extrapolated by means of the latter diverge from, and are inherently less probable than, those derived from the former, especially at temperatures above 1000°.

GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTE OF WASHINGTON,
WASHINGTON, D. C.

ON THE CONDUCTIVITY OF SOME CONCENTRATED AQUEOUS SOLUTIONS AT ZERO.

BY W. H. SLOAN.

Received May 9, 1910.

As a preliminary step to an investigation of the conductivities of certain salts in mixed solutions of water and ammonia, some measurements were made of the conductivity of potassium iodide in concentrated aqueous solutions, which gave unexpected values. Further investigation confirmed these results, and the measurements were extended to potassium bromide, sodium nitrate, ammonium nitrate, silver nitrate, and copper

Potassium iodide.

Log φ/1000.	φ/1000.	A.	Log. φ/1000.	φ/1000.	A.
9.2470	0.1766	57.45 57.15	0.4242	2.651	70.96 70.70
9.2659	0.1845	59.17	0.5211	3.32	71.56
9.3170	0.2075	64.33	0.6180	4.150	72.03
9.3570	0.2371	65.20	0.7252	5.31	72.36
9.4419	0.2760	67.83	0.8928	7.812	73.13
9.4420	0.2767	67.60 67.70	1.0262	10.62	74.13
			1.1232	13.28	74.55
			1.3273	21.25	75.60
9.5211	0.3326	69.43 69.20			
9.6180	0.4150	70.56 70.50 70.25			
9.7430	0.5534	71.00 70.65 70.77			
9.8222	0.664	70.43			
9.9191	0.830	70.70 70.53			
0.1232	1.328	70.46			
0.2201	1.660	70.60 70.70			

Potassium bromide.

9.4523	0.283	65.7
9.5704	0.3717	67.30
9.8714	0.7435	68.63
0.1724	1.487	69.35
0.4734	2.975	70.10
0.7745	5.95	72.50
1.0755	11.90	74.65

Ammonium nitrate.

9.0706	0.1177	31.22
9.3011	0.200	45.01
9.6021	0.400	54.05
9.9031	0.800	58.36
0.2042	1.600	61.20
0.5052	3.200	64.41
0.8062	6.400	66.87
1.1072	12.800	69.72
1.4085	25.61	71.45

Silver nitrate.

9.3273	0.2125	25.70
9.4242	0.266	28.76
9.7253	0.531	37.22
0.0263	1.067	44.46
0.3273	2.125	50.56
0.6283	4.250	55.40
0.9294	8.500	59.75
1.2304	17.00	63.10

Sodium nitrate.

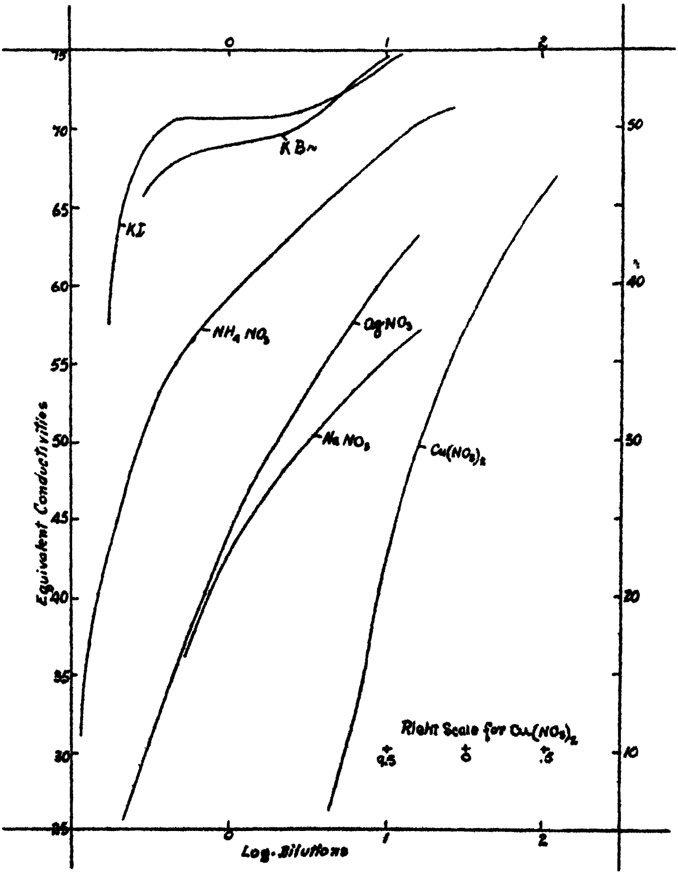
9.7253	0.531	36.41
0.0263	1 0625	43.20
0.3273	2.125	47.81
0.6284	4.250	51.50
0.9294	8.50	54.72
1.2304	17.00	57.41
..	...	...
..	...	...

Copper nitrate.

Log. φ/100.	φ/1000.	A.	K (spec. cond.)
9.1143	0.130	5.65	44.58
9.1600	0.144	7.42	51.36
9.2692	0.186	12.26	66.01
9.4153	0.2602	18.98	72.96
9.7165	0.5206	30.33	58.28
0.0175	1.041	37.90	36.41
0.3190	2.084	43.20	20.73
0.6207	11.32	47.00	11.32

nitrate. Of these, the potassium bromide resembles the potassium iodide to some extent, but its limited solubility prevented measurements of any concentrated solutions. The other salts gave no exceptional values, save in the case of copper nitrate, where in the concentrated solutions, the specific conductivity of the solution increased from a dilution of 0.13 up to 0.26 and then fell off again. (See table Copper nitrate).

The measurements were made by means of a wire bridge and a Kohlrausch conductivity cell. A large Dewar tube was used for a thermostat, which was filled with crushed ice and water. With the use of a stirrer, a very constant temperature of 0.05° to 0.1° + was easily maintained.



(This type of thermostat was first used on account of the special type of cell necessary in the conductivity measurements of the ammonia solutions. The use of the Dewar tube made the reading of the volumes possible from the outside).

The water used was twice distilled, first from dilute sulphuric acid and potassium dichromate, and then from a barium hydroxide solution. The salts used were of Baker's Special Analyzed Chemicals, and in the case of the potassium iodide, the measurements were checked against a recrystallized sample. In every case several readings were taken on the bridge, and in the case of the potassium iodide, four different samples of salt, and three different cells were used, all giving check results.

The above results were obtained where Λ = equivalent conductivity and $\phi/_{1000}$ = dilution.

In plotting the curves, the logarithms of the dilutions were used.

The results obtained for the concentrated solutions of potassium iodide are decidedly different from those given by Jones and Douglas,[1] but the type of curve agrees very closely with that of Kahlenberg,[2] the molecular conductivity being a little higher than Kahlenburg's.

In plotting the conductivities of potassium iodide and potassium bromide at 18°, on the same basis, the values as given by Kohlrausch and associates, show the same tendency, but not so marked, but the concentrations are not so great.

The values at 0° for potassium iodide resemble in some respects, the conductivities of certain salts in methylamine and liquid ammonia, as given by Franklin and Gibbs[3] and Franklin.[4]

A satisfactory explanation of the results obtained does not seem possible at present. It is hoped that further measurements may produce some clue.

This work was carried out at the suggestion and under the direction of Prof. E. C. Franklin.

STANFORD UNIVERSITY, CALIFORNIA.

[FROM THE INSTITUTE OF ANIMAL NUTRITION LABORATORY, STATE COLLEGE, PA.]

ELECTRIC COMBUSTION FURNACE FOR METHANE DETERMINATION.

BY J. A. FRIES.

Received June 13, 1910.

In connection with the respiration calorimeter experiments upon cattle which are being carried on here, it is necessary to determine the amounts of combustible gases (consisting chiefly or wholly of methane) excreted. For this purpose an electric combustion furnace has been in use in this laboratory during several periods of 50 consecutive hours each, and is giving perfect satisfaction.

---

[1] *Am. Chem. J.*, 26, 445. Calculated to reciprocal ohms, Tower's "Conductivity of Liquids."

[2] *J. Phys. Chem.*, 5, 348.

[3] THIS JOURNAL, 29, 1389.

[4] *Z. physik. Chem.*, 69, 272.

The work to be done and the size and construction of the furnace are so different from those of ordinary combustion furnaces that a description of the furnace may not be without interest and value.

Work Required of the Furnace.—From the continuous current of air passing through the respiration calorimeter chamber when an experiment is in progress, samples for analysis are taken at frequent and regular intervals, the quantity of these samples being equal to a continuous air current of 3.5 liters per minute. This amount of air passes through the combustion tube, where the combustible gases are oxidized, platinized kaolin serving as a catalyzer.

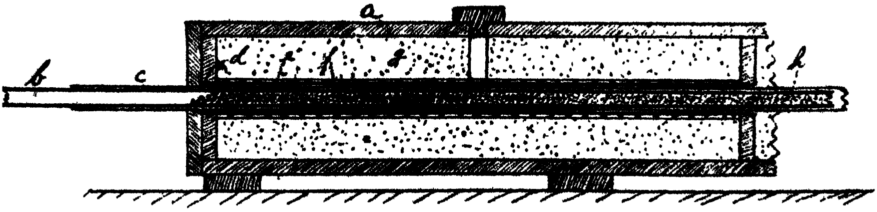
Combustion Tube.—The combustion tube, which is similar to that used previously with a gas furnace for the same purpose during a number of years, is a seamless copper tube 3.35 meters long, $^3/_4$ inch iron pipe size, inside diameter about 20 mm., and with walls about 3 mm. thick. The heated section of this copper tube is protected by a nickel-plated brass tube 8 feet long which fits loosely over it.

Electric Current.—The electric current at our disposal is a three-phase alternating current of about 110 volts pressure during the day, but in the evening and night when the most lighting is required, the voltage is increased to between 120 and 125.

Material for Furnace.—The outside box and supports for the tubes were $^3/_4$ inch thick asbestos lumber. Three quartz tubes, 37 mm. inside diameter, each about 70 cm. long, were used for cores upon which were wound the resistance coils, consisting of 6 mm. Nichrome ribbon. A 3 mm. asbestos cord and an 18 mm. asbestos tape were used to keep the resistance coil in position and prevent short circuiting.

Construction of the Furnace.—The accompanying sketch of a section of the furnace shows the construction of the same.

The outside dimensions of the asbestos box are: 215 cm. long, 17.5 cm. wide, and 19 cm. high. The asbestos was worked and screwed together like ordinary wood. Cross partitions supporting the ends of the quartz tubes were securely fastened to the sides of the box. Each quartz tube was wound separately with about 4 meters of Nichrome ribbon 6



Cross-section showing one-third of the furnace: *a*, asbestos lumber; *b*, copper tube; *c*, brass tube; *d*, quartz tube; *e*, Nichrome ribbon; *f*, asbestos tape; *g*, quartz sand; *h*, platinized kaolin.

mm. wide and 0.3 mm. thick, having a resistance of 173 ohms per 1000 feet. This length made a coil of 29 turns equally spaced over the exposed length of the tube. The ribbon was wound directly on the quartz tube, wired fast with resistance wire at each end, and between each turn was wound a 3 mm. asbestos cord. Between the turns of the cord an 18 mm. asbestos tape was wound directly over the Nichrome ribbon. This method of winding made it all very firm and practically impossible for the ribbon coils ever to work loose and the loops to come in contact with each other. The wound quartz tubes were put in position so that they formed a straight opening. The ends of the coils leading out to the binding posts on the outside of the asbestos box were doubled back upon themselves twice and wired together, in order to reduce the resistance and the heating of them by the current. Very thin asbestos was laid over joints and any crack in the asbestos tape winding so as to keep the sand away from the tubes, and then the box was filled with fine quartz sand. About the middle of each tube and coil there was left a round hole, 1 inch in diameter, extending from the outside of the lid to the asbestos covering on the ribbon, and by means of this opening the condition of the tubes as to heat can be observed at any time. The binding posts were screwed on the side of the box and the doubled up ends of the ribbon project between the lid and upper edge of the side of the box. Three of these binding posts connect the three main wires and the three ends of the resistance coils. The coils themselves were connected in star fashion, that is, the three free ends were united.

This method of wiring reduces the voltage in the coils and hence less ribbon is required per coil for a given amount of heat than by the mesh method of wiring. The maximum heat possible under this system of wiring would be

$$\text{main voltage}/\sqrt{3} \times \text{amperes}.$$

By actual test the voltage across these resistance coils varied from 60.5 to 62.5, and the ammeter measured about 23.5 amperes, while at the same time the voltage between the three mains was 107.5 to 108.5. The load on the main was not perfectly balanced nor was the current very steady, but from the average of the readings, the heat generated in each coil would be 1434 watts, or computed to the surface of the tube, equal to 1.7 watts per square centimeter.

This amount of heat proved to be entirely too much and the temperature of the furnace rose to nearly 1200°. The greater efficiency noticed in this furnace, when compared with the results of laboratory tests made with quartz tubes wound with wire and insulated with magnesia covering, must be ascribed to the better insulating quality of the sand, and to the fact that a broad ribbon was used for resistance coils instead of a small wire.

In order to reduce the heat in the furnace, a coil consisting of 5 feet of the same ribbon was put in as outside resistance in each of the three main wires and in order to meet the fluctuations and increase in voltage on the main, two sets of coils, 1 foot ribbon per coil, were so arranged on the top of the box that one or both sets could be thrown in by means of two switches. Each of these sets of coils equals about 1 ampere difference in the current.

By this arrangement of the resistance, the current can be held at 15 to 15.5 amperes, which maintains a temperature of 700° or a little less in the furnace. This is equivalent to about 0.79 watt per square centimeter tube surface. With the copper combustion tube in position, the temperature of the furnace is reduced somewhat near the ends of the furnace, but under these conditions the heat has been found to be sufficient for the work required.

The ends of the copper combustion tube were threaded and reduced to $^1/_4$ inch iron pipe size by means of brass fittings, the joints of which were also soldered. The return pipe from the furnace to the train of absorption tubes is iron connected with good rubber tubing.

Test of the Furnace and Combustion Tube.—When all connections had been made ready for use the whole system was put under 5 inches mercury pressure and suction and showed no leak. Next, the oxidation capacity of the furnace was tested by allowing alcohol vapor to be carried through with the air current, the carbon dioxide formed being absorbed and the air again allowed to pass through a similar combustion tube heated by gas. It was found that the combustion was perfect in the electric furnace, not a trace of carbon dioxide being found after the second furnace.

After this test a weighed quantity of alcohol was oxidized with the following results:

		CO_2.	H_2O.
5.4127 grams alcohol, sp. gr. 0.82478:	Theoretical,	9.2271 g.	6.2542 g.
	Found.	9.2210 g.	6.1920 g.

The carbon dioxide found agrees as well as can be expected with the theoretical, but the water is a little low. This was caused by stopping the experiment a little too soon, some of the water still remaining condensed in the connections. The time used for the determination was $3^1/_2$ hours. This test was considered entirely satisfactory and the furnace has proven so ever since.

Expansion of Copper Tube.—The copper combustion tube expands about 1 inch in length when heated, besides a very small amount in diameter, hence it should not fit too tightly in the furnace, nor have very sharp edges nor rough surfaces over which to move. Because of this expansion it is advisable to use rubber connections at the cool ends or some flexible tin or lead pipe where such material can be used. The small unevenness commonly found in the quartz tubes does not seem to interfere with the expansion.

Durability of Copper Combustion Tube.—Copper tubes such as have been described have been in use with the gas furnace for as many as 1100 hours before being renewed. With the electric furnace, where the heat is much more uniform, the tube, which in this case is nickel-plated on the outside, may last even longer.

Advantage of Electric Furnace over the Gas Furnace.—By the electric furnace a source of probable error—that of combustible gases under certain atmospheric conditions contaminating the air supply of the respiration calorimeter—has been removed. It supplies more uniform heat. It is more economical than gasoline gas since even with much outside resistance the amount of heat lost is only a very small fraction of that wasted by a large gas furnace. There is no trouble in regulating the heat as there is with a varying gas supply.

THE PRECIPITATION OF THE IRON GROUP AND THE COMPOSITION OF CERTAIN FERRIC FORMATES.

By O. F. Tower.

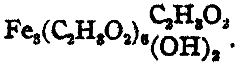
Received June 7, 1910

The difficulties of precipitating the metals of the iron group, *viz.*, iron, aluminium and chromium are well known. Many prefer to attempt no independent separation, but to precipitate them along with the zinc group by using both ammonium hydroxide and ammonium sulphide. This, however, entails a complex and rather tedious method of analysis, unless chromium is known to be absent. In case manganese is absent the metals of the iron group may be separated rather sharply by repeating the process of precipitation. After the first precipitation with ammonium hydroxide, the precipitate is dissolved in hydrochloric acid and the metals reprecipitated with ammonium hydroxide as before. In this way any zinc or nickel dragged down in the precipitation are fairly completely removed. The most complete method of separation, however, no matter what other common metals may be present, is to precipitate them as basic acetates. Furthermore, the presence of PO_4''' causes no complications when the basic acetate process is employed, provided sufficient $\overset{\cdots}{Fe}$ is present. In addition to causing the removal of the PO_4''', $\overset{\cdots}{Fe}$ is required to insure the precipitation of chromium. The great objection to the use of the method, however, is the great difficulty experienced in filtering and washing the precipitate of basic acetates.

On this account, in 1861, F. Schulze[1] recommended the use of ammonium formate for precipitating iron and aluminium, claiming that the basic formates are much easier to filter and wash than the corresponding acetates. This paper contains an account of an investigation of this point together with a few matters closely related to it.

Schulze's conclusions, in the main, have been confirmed. Both iron and aluminium can be practically completely precipitated by boiling with ammonium formate provided the solution is sufficiently dilute. The boiling need be continued only for a moment. The precipitate has a flocculent appearance and looks as if it could be filtered with great ease. Filtration is, however, not so rapid as Schulze describes, but can be accomplished in less time than in the case of the basic acetates. Chromium by itself is not precipitated by boiling with ammonium formate, but is carried down by basic ferric formate, hence the presence of $\overset{\cdots}{Fe}$ is required for the complete precipitation of the group. The presence of ammonium chloride is desirable, as it causes the precipitate to be thrown down in larger flakes, which facilitates filtration.

The procedure found to give the best results follows: After hydrogen sulphide has been expelled from the filtrate of the copper-tin group and iron, if present, has been oxidized (if Fe is not present, 5–10 cc. molar $FeCl_3$ must be added), add ammonium chloride, and then dilute the solution until the concentration of any one of the metals of the iron group does not exceed 1/100 molar, and heat the whole to boiling. Add about 10 cc. 4 *N* ammonium formate and continue to boil for about one minute. Filter hot, preferably with the suction pump. The group is then analyzed as usual, except that, of course, iron must be tested for in the original solution, or at least before the precipitation of the group.



The question arose as to the nature of the precipitate and the composition of the ferric formates in general. This is especially interesting in view of the recent work of Werner and his associates on the acetates of the metals of this group[2] and on the formates of chromium.[3] For example, Weinland and Gussmann[4] have been unable to isolate ferric triacetate by any of the methods given for its preparation. There crystallizes usually from strongly acid solutions containing ferric hydroxide and acetic acid a basic salt of a triferric base, *viz.*, $Fe_3(C_2H_3O_2)_6{}^{C_2H_3O_2}_{(OH)_2}\cdot H_2O$, the formula indicating that only one acetate radical is replaceable. Another acetate containing one less hydroxyl group than this was also prepared. The formula of basic ferric acetate is commonly given as $Fe(OH)_2C_2H_3O_2$. But the basic acetate precipitated in the usual manner was found to correspond to the formula $\begin{bmatrix} C_2H_2O_2 \\ Fe_3(OH)_2 \\ O_3 \end{bmatrix}$, or, if the three iron atoms do not remain together, it may be written $Fe_2O_3.Fe(OH)_2C_2H_3O_2$ or

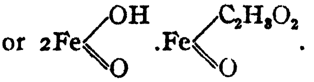
---

[1] *Chem. Centralblatt*, 1861, 3.

[2] See *Ber.*, 41, 3236 and 3447 (1908); 42, 2997 and 3881 (1909); *Z. anorg. Chem.*, 66, 157 (1910).

[3] Werner, *Ber.*, 41, 3449 (1908).

[4] *Ber.*, 42, 3881 (1909); and *Z. anorg. Chem.*, 66, 157 (1910).



Ludwig[1] and also Scheuer-Kestner[2] claim to have prepared ferric triformate by allowing formic acid to act upon moist ferric hydroxide, the acid being present in large excess, crystals of the salt appearing after gradual evaporation. It was, however, found to be impossible to obtain the triformate by this or any of the other processes tried.

Ferric hydroxide was prepared by neutralizing ferric chloride with ammonium hydroxide, the precipitation being carried out at great dilution and both hot and cold. When precipitated in the cold ferric hydroxide dissolves readily in excess of cold formic acid; precipitated hot, it dissolves very slowly, but may be made to dissolve completely by continued agitation. When ferric hydroxide is boiled with excess of formic acid, complete solution does not take place. For the following experiments a paste of well washed ferric hydroxide and water was prepared, which contained about 1 mol. per liter. The formic acid used was a Kahlbaum preparation and had a specific gravity of 1.22.

A certain volume of the ferric hydroxide paste was treated with an equal volume of the formic acid, and the mixture shaken until complete solution took place. Whether evaporated in the air or under a desiccator, crystals were deposited upon the sides of the containing vessel. These were collected and kept in a desiccator over soda-lime for several days to remove the last traces of acid and then were transferred to one containing sulphuric acid, where they remained until analyzed. The mother liquor from these also deposited a good crop of fine crystals on the bottom of the containing vessels, which were dried in the manner just described. Formic acid was determined by treating a weighed quantity of the crystals with excess of 0.5 *N* sodium hydroxide, heating carefully for 15 minutes, letting cool, and transferring to a graduated cylinder. After the ferric hydroxide had completely subsided, an aliquot portion of the supernatant liquid was drawn off and titrated with 0.2 *N* hydrochloric acid. The method was rapid, although not very accurate, but sufficiently so for the present purpose. Iron was determined by filtering off the ferric hydroxide remaining in the cylinder, washing with hot water free from alkali, and weighing the residue in a platinum crucible. The accompanying table gives the results of the analysis of crystals obtained in all the ways mentioned above. It will be observed that they were of uniform composition, and that this composition does not correspond to the formula of the triformate but to that of a basic

---

[1] *Arch. Pharm.*, [2] 107, 1 (1861).

[2] *Compt. rend.*, 56, 1092 (1863).

Fe. Per cent.	CHO_2. Per cent.	
31.2	60.6	Required for $Fe(CHO_2)_3$, Fe 29.3 per cent., CHO_2 70.7 per cent.
31.5	61.5	
34.0	60.5	
32.4	60.2	Required for $Fe_3\substack{(CHO_2)_7\\(OH)_2}$, Fe 32.4 per cent., CHO_2 61.0 per cent.
33.2	59.6	

salt of a triferric base of the same composition as the acetate precipitated under similar conditions except for the molecule of water of crystallization. Various modifications of the process outlined above were tried but no normal ferric formate could be obtained.

The formate obtained dissolves very slowly in cold water, more rapidly in warm. The salt cannot be obtained again from the solution, as a more basic salt described below was the only one deposited. It also dissolves slowly in formic acid. Neither the acid nor the aqueous solution gives a precipitate with chloroplatinic acid, and no evidence has yet been obtained to show that one, and only one, of the CHO_2 radicals is ionized as was found by Weinland and Gussmann to be the case with the corresponding acetate.

When ammonium formate in excess is added to ferric chloride solution the liquid becomes dark red and on warming deposits a brown flocculent precipitate. This precipitate was filtered out, washed, dried and analyzed in the manner just described. The results of the analysis are shown in the accompanying table. The composition of the precipitate is evidently that of the second formula and is therefore analogous

Fe. Per cent.	CHO_2. Per cent.	
57.0	15.1	Required for $Fe(OH)_2CHO_2$, Fe 41.4 per cent., CHO_2 33.4 per cent.
56.4	14.8	
57.1	14.8.	Required for $\left[\begin{matrix}CHO_2\\Fe_3(OH)_2\\O_3\end{matrix}\right]$, Fe 56.5 per cent., CHO_2 15.3 per cent.

in composition to the basic acetate thrown down under similar conditions.

Whether ammonium chloride is present or not during the precipitation makes no difference in the composition of the precipitate. When a mixture of ferric chloride and ammonium formate in excess stands at ordinary temperature for several days an amorphous precipitate is deposited whose composition in the samples investigated does not correspond to that of the basic salt just described, as can be seen from the following table. The substance is richer in formate than the one precipitated hot. It corresponds somewhat closely in composition to the formula of a basic diformate, but I incline to the belief that it is a mixture of the basic monoformate with a small quantity of some formate richer in formic acid.

Fe. Per cent	CHO_2 Per cent
53 0	17 2
51 6	18 5
50 7	19 3

Required for $\left[Fe_3\begin{matrix}(CHO_2)_2\\OH\\O_3\end{matrix}\right]$, Fe 51.9 per cent, CHO_2 27 9 per cent

Summary.

1. The iron group may be precipitated as basic formates, which filter somewhat more readily than the basic acetates.

2. The presence of iron is necessary for the precipitation of chromium.

3. It was found impossible by any of the methods heretofore described to prepare normal ferric formate. In its place was always obtained a good crystalline precipitate corresponding to the formula $Fe_3\begin{matrix}(CHO_2)_7\\(OH)_2\end{matrix}$.

4. The basic formate precipitated under the usual conditions possesses a composition expressed by the formula $\left[Fe_3\begin{matrix}CHO_2\\(OH)_2\\O_3\end{matrix}\right]$.

WESTERN RESERVE UNIVERSITY, CLEVELAND

A RAPID AND ACCURATE METHOD FOR THE DETERMINATION OF TITANIUM.

BY O L BARNEBY AND R M ISHAM

Received May 2, 1910

Having a number of determinations of titanium in rutile and iron ores to make and failing to obtain consistent results by use of the common methods the authors proceeded to investigate for a shorter yet accurate process for this determination. Low's method[1] adapted from Blair gives good results, but requires too much time for the ordinary analysis. This method was used in checking three series of analyses. Gooch's method was not tried as it seemed to have the same disadvantage as the other methods—requiring too much time to obtain a pure product of weighable titanium oxide.

Methods depending on the precipitation of titanic acid in boiling solutions containing sulphurous and sulphuric acids gave low results. Those requiring SO_2 or H_2S reduction of the iron and precipitation of the titanium with ammonia or by boiling with sodium or ammonium acetate and acetic acid were found to give high results when a large excess of iron was present, and required repeated treatments to completely remove the latter element.

---

[1] Low's "Technical Analysis of Ores," p. 189.

This accords with the results of Blair,[1] Fresenius,[2] and others. Pisani's[3] volumetric method, modified by Wells and Mitchell,[4] reducing the titanium from $TiCl_4$ or $Ti(SO_4)_2$ by zinc in the presence of free acid and titrating with potassium permanganate in an atmosphere of carbon dioxide failed to give accurate results. In no case where considerable titanium was present was the reduction absolutely complete and frequently the results were from 5–10 per cent. low after prolonged reduction by the zinc. This is in accordance with the published work of Wells and Mitchell[5] on the application of this method.

Rothe's method[6] for the removal of the iron from titanium in the determination of the former, used likewise by Noyes, Bray and Spear[7] to separate titanium and zirconium from iron and thallium in their System of Qualitative Analysis finds application in removing most of the iron quickly. The method attributed to Ledebur by Classen[8] for pig iron analysis will not give good results due to the presence of titanium in the silica and graphite which is discarded, the solubility of titanic acid in hydrochloric acid, and the contamination of the final product by foreign elements such as aluminium.

The method as outlined below is based on the volatilization of the silica by hydrofluoric acid in the presence of sulphuric acid, evaporation to dryness and fusion with sodium carbonate and a little sodium nitrate to convert the iron and titanium to insoluble ferric oxide and sodium titanate, extraction with hot water to remove the soluble phosphates, sulphates and aluminates; solution of the ferric oxide and sodium titanate in hydrochloric acid, extraction of ferric chloride with ether; reduction of slight traces of iron with sulphur dioxide; precipitation of the titanic acid by boiling in acetic acid solution, filtration and ignition to titanium oxide (or colorimetric). (If the directions as given are strictly followed usually the sulphur dioxide reduction may be omitted as the iron will have been completely removed.)

The weighed sample in a platinum crucible is moistened with water, 5–10 drops concentrated sulphuric acid, and 1 cc. of hydrofluoric acid are added, and the mixture heated on an asbestos hot plate until cessation of sulphur trioxide fumes. Five or ten grams of sodium carbonate and a little sodium nitrate are added and the mixture fused at least 30 minutes. The crucible and cover are cooled, placed in a beaker, covered with hot water and heated until the melt is disintegrated. Ferric oxide and sodium titanate are left in the residue insoluble in hot water. The crucible is removed, washed and any adhering particles of ferric oxide and sodium titanate are dissolved out with hot hydrochloric acid (sp. gr. 1.11). These solutions are saved. The residue in the beaker is filtered and washed with hot water. The filter is perforated and the residue carefully washed down into a clean beaker with hydrochloric acid (sp. gr. 1.11). The hydrochloric acid washings from the platinum crucible are transferred to the beaker and the whole heated on the hot plate until solution is complete and volume is reduced to 15-20 cc. The solution is cooled, 2 cc. of concentrated hydrochloric acid added, and transferred to a separatory funnel, the beaker being rinsed with hydrochloric acid (sp. gr. 1.11). An equal volume of ether, which has been previously shaken with concentrated hydrochloric acid, is added to the solution, a rubber stopper is inserted in the top, the funnel is inverted, the stopcock opened and the whole thoroughly shaken. The stopcock is then closed and the funnel placed in an upright position and allowed to stand 10 minutes. The aqueous layer is drawn off into another separatory funnel. The ether is rinsed twice by shaking well with 5-10 cc. portions of hydrochloric acid (sp. gr. 1.11) and the washings added to the aqueous solution. (The ether is run off into an ether residue bottle and saved for purification.) The treatment with ether is repeated two or three times until the ether layer no longer shows any greenish tinge due to the presence of dissolved iron. The aqueous solution is then transferred to a beaker and 3-5 cc. of hydrogen peroxide added. If the solution does not develop a fairly intense color the titanium may be determined colorimetrically by the method given below.

---

[1] Blair's, "Chem. Anal. of Iron," p. 180.

[2] Fresenius-Cohn, *Quant. Chem. Anal.*

[3] *Ibid.*, Vol. 1, 285.

[4] This Journal, 17, 878.

[5] *Loc. cit.*

[6] *Mitth. Köngl. tech. Vers.*, 10, 132; *Stahl und Eisen*, 12, 1052; 13, 333.

[7] This Journal, 30, 515.

[8] Classen's, "Ausgewählte Methoden der Anal. Chemie," p. 501.

If an intense color develops the solution is heated to expel dissolved ether, 10 cc. of concentrated sulphuric acid are added and the solution evaporated to sulphur trioxide fumes. The cooled solution is diluted to about 100 cc. (any platinum present should be precipitated by hydrogen sulphide at this point) and the solution nearly neutralized with ammonia. One or 2 grams of ammonium bisulphite are added and the solution warmed on the hot plate for half an hour. Ten to 15 grams of ammonium acetate are added and 5-10 cc. of glacial acetic acid and the solution boiled for 15 minutes. Filter. The precipitated titanic acid is filtered off washed with dilute acetic acid (not over 11 per cent.), ignited and weighed as titanium oxide.

In case the hydrogen peroxide test as performed above indicates the presence of only a small amount of titanium the quantity may be determined colorimetrically. Heat the solution to expel dissolved ether, cool, transfer to a Nessler's tube, treat with 4-5 cc. of hydrogen peroxide, dilute to 100 cc. and determine by comparison with measured quantities of a standard solution of titanic acid in hydrochloric acid, which have been subjected to the same peroxide treatment. This comparison can be most conveniently carried out by adding the standard solution, drop by drop from a burette, to a Nessler's tube containing hydrogen peroxide and hydrochloric acid and made up to near the 100 cc. mark. The solution should be agitated from time to time and the process continued until an equivalent color is developed.

In following out this method as outlined three ores were used. Sample A was a sample of rutile from Kahlbaum, sample B was a specimen of concentrates from a Virginia ore, and sample C was a titanium iron ore from Lower Canada. These ores were analyzed by the method given above and the results checked by use of the method proposed by Low. The results obtained are tabulated in the following table.

Sample.	Method.	Wt. Samples.	Wt. TiO_2 + Fe_2O_3 1st ppt. by Low.[1]	Final wt. TiO_2.	Per cent. TiO_2.	Average per cent
				0.1652	82.60	
				0.1650	82.50	
A...	Authors' method....	0.2		0.1652	82.60	82.58
				0.1653	82.65	
				0.1651	82.55	
	Low's method.......	0.2	0.1782	0.1652	82.60	82.67
			0.1694	0.1655	82.75	
				0.1776	88.80	
B...	Authors' method....	0.2		0.1774	88.70	88.68
				0.1771	88.55	
	Low's method.......	0.2	0.1772	0.1772	88.60	88.55
			0.1770	0.1770	88.50	
				0.0785	15.70	
C...	Authors' method....	0.5		0.0785	15.70	
				0.0781	15.62	15.67
				0.0783	15.66	
	Low's method.......	1.0	0.1618	0.1552	15.52	15.51
			0.1708	0.1550	15.50	

In a preliminary effort to show the quantitative nature of the ether separation the following experiments were performed: I. A solution of titanic acid in hydrochloric acid was standardized by precipitation with ammonium hydroxide and ignition to titanium oxide. II. Blanks were run, carrying 10 cc. portions of the titanium solution through three ether separations with final precipitation with ammonium hydroxide. III. Separations were run by mixing 10 cc. portions with 5 cc. of a saturated ferric chloride solution and subjecting the mixture to the regular ether treatment with sulphur dioxide reduction and ammonium acetate precipitation.

---

[1] Using Low's method whenever iron was present it was found necessary to refuse and reprecipitate to free the titanium oxide from ferric oxide.

I (*a*) 0.1140	II (*a*) 0.1142	III (*a*) 0.1141
(*b*) 0.1139	(*b*) 0.1144	(*b*) 0.1140
		(*c*) 0.1141

It is suggested that for the analysis of pig iron, steel, etc., a 5–10-gram sample be dissolved in 30–40 cc. of concentrated hydrochloric acid to which 4–5 cc. concentrated nitric acid has been added, and the solution evaporated to the consistency of sirup. Add 1–2 cc. of concentrated hydrochloric acid, take up with 20 cc. of hydrochloric acid (sp. gr. 1.11), and filter. Transfer the filtrate to a separatory funnel and the residue to a platinum crucible.

After one treatment with ether as given above, the aqueous solution should be treated with ammonia, the precipitate filtered out and added to the residue in the platinum crucible. Ignite filter paper, treat with hydrofluoric acid, fuse, and complete the determination as previously given.

We note that in the original colorimetric work of Weller,[1] as well as in all subsequent modifications, the titanium was oxidized in the presence of sulphuric acid. For the sake of comparison equivalent solutions of titantium in sulphuric and in hydrochloric acid were prepared. We found that the color developed by oxidation was fully as intense and stable, in hydrochloric as in sulphuric acid. Inasmuch as solutions containing 1 mg. or more of titanium developed a somewhat higher color with hydrochloric acid it is advisable to use a standard solution of titanium in hydrochloric acid for the comparison.

Observing the aqueous titanium solution in the ether extraction to be colorless if peroxide-free ether is used led us to doubt the formation of a "yellow-white compound" with ether described by Rosenheim and Schütte.[2] These authors write: "The yellow-white, very indistinctly micro-crystalline mass, which remains after the action of hydrochloric acid and ether on titanium hydroxide, was almost completely soluble in cold water and precipitated gelatinous titanic acid on boiling." Treating titanium hydroxide in all degrees of hydration with several proportions of hydrochloric acid in ether gave no color mentioned above provided the last trace of peroxide was removed from the ether. If even a small amount of peroxide was present, Rosenheim and Schütte's observations were confirmed.

Conclusions.

1. The volumetric method based on the reduction of titanium to the tri-valent state and oxidation with permanganate gives low results.

2. With the sulphur dioxide reduction when considerable iron is present the titanium product is usually contaminated with some iron.

---

[1] *Ber.*, 15, 2593.

[2] *Z. anorg. Chem.*, 26, 241.

3. The ether separation removes practically all the iron from the titanium very quickly.

4. Refusion of the ignited product with sodium carbonate for purification, which requires considerable time, is never necessary by use of this method. The final product is pure, unless zirconium is present, in which case this element is removed by the usual phosphate precipitation.

5. This method combines the colorimetric and gravimetric determinations and the color comparison is made in solutions always totally free from iron. For convenience hydrochloric rather than sulphuric acid solutions of titanic acid are used.

6. The method is accurate and not long.

7. Rosenheim and Schütte's yellow compound probably owes its color to the presence of peroxides in the ether used.

UNIVERSITY OF NEBRASKA,
LINCOLN.

APPARATUS FOR THE DETERMINATION OF ARSENIC.

BY OTIS D. SWETT.

Received May 28, 1910.

The many existing forms of apparatus for the determination of arsenic which give trustworthy results appear to have left little to be sought for with regard to this most essential feature. The more or less complex construction of these forms, however, together with the sources of error which usually accompany such construction, seem to justify an attempt to devise an apparatus for arsenic determination which, besides yielding accurate results, shall comprise fewer parts than are found in the other forms, and shall be compact and portable.

With these points in mind, an apparatus has been devised which is illustrated in the accompanying drawing.[1]

A is a round wooden base with a central depression and three vertical lugs which form an extension of the sides of the depression.

B is a glass vessel, 4 cm. outside diameter and 14 cm. long, with flat closed bottom, supported by the base *A* in the depression between the vertical lugs. The vessel *B* is provided with a lower side tube *b*, projecting beyond the base *A* between the vertical lugs, and with the upper side tube *b'*.

C is an inner tube, 18 mm. outside diameter, closed at its lower end, enlarged conically at its upper open end, rolled out and sealed to the top of the vessel *B*, which is closed in to meet it, and then ground on its inner surface to receive a stopper.

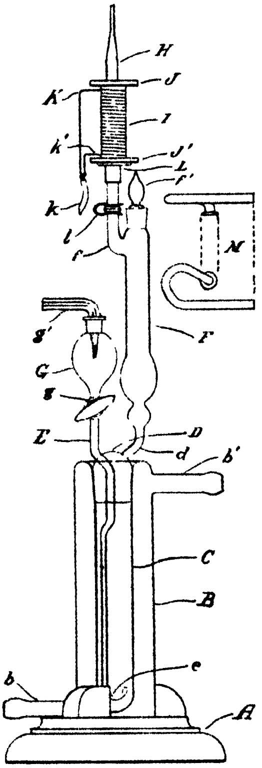
D is a hollow stopper with dome-shaped closed top, tapering to the other end, which is open, and ground to fit the neck of the inner tube *C*.

---

[1] Glass work by Mr. Edw. O. Sperling, Bureau of Standards.

F is a vertical drying tube, with the usual enlargement and moisture bulb, communicating with the interior of the stopper *D* through the offset tube *d*.

f is a side tube, extending laterally from near the top of the drying tube to the vertical axis of the apparatus, then vertically to the top level of the drying tube, flattened and ground to fit the correspondingly flattened and ground ignition tube *H*.



f' is a light ground glass stopper fitting the ground open end of the drying tube.

E is a tube passing through, and sealed to, the top of the hollow stopper *D*, and extending within the inner tube *C* to near the bottom, where it terminates in a gas trap, *e*, and extending upwards from the hollow stopper *C*, with an offset bend, to the stopcock *g* and communicating through this with the 5 cc. funnel *G*, which is closed in at the top to a small neck ground to take the enlarged and suitably ground capillary tube *g'*, this latter being drawn out somewhat smaller at the lower end, bent at right angles above the funnel neck, and so shaped at the outer end as to accommodate a rubber tubing.

H is a hard glass tube 6–4 mm., drawn out at one end in a suitable manner for the production of the mirror, and flattened and ground at the other end to fit the similarly finished end of the side tube *f* as described.

I is a heating coil, consisting of a threaded spool of "lavite"[1] 12 mm. outside diameter and 8 mm. inside diameter, wound with number 26 "Advance" resistance wire,[2] and mounted with a shield disc *J*, of the same material which prevents the tube above from becoming overheated.

J' is a "lavite" disc similar to *J*, upon which the heating tube *I* rests.

K, *K'* are the conducting wires and *k* is the two-wire insulated conductor from which they project.

L is a metallic sleeve, fitting snugly over the ignition tube *H*, cut to form spring fingers bearing firmly upon the ignition tube, and carrying, as an integral part, a disc which forms a flange around the upper end of the sleeve, thereby providing a means for supporting and vertically adjusting the heating coil *I*.

[1] Manufactured by the D. M. Steward Mfg. Co., Chattanooga, Tenn.

[2] Manufactured by the Driver-Harris Wire Co., Harrison, Newark, New Jersey.

l is a clip, adapted to hold firmly together the flattened and ground ends of the side tube *f* and ignition tube *H*.

M is a glass tube 5 to 7 mm. inside diameter made to fit the flattened and ground end of the tube and bent horizontally to keep within the radius of the apparatus.

The ignition tube first employed was of transparent silica, mounted by a short mirror tip. The metal clip being above the heating tube, and not thoroughly shielded from the heating coil, gave rise to irregular mirrors. When a tube, however, is used for both ignition and deposition, a number of such tubes must be on hand when making up a set of standards and for consecutive analyses, so that silica, on account of its cost, is barred. Instead, Jena boro-silicate glass, or indeed a high quality combustion glass, may be used.

A modified form of the vessel *B* has been designed, which is essentially an Erlenmeyer flask, provided with side tubes and carrying the sealed-in tube *C*, thereby eliminating the wooden base, and providing space for a larger reaction vessel.

With slight modifications this apparatus is adapted for use with many methods heretofore proposed.

For the Marsh,[1] Berzelius-Marsh,[2] and Sanger-Berzelius-Marsh[3] methods, the drying tube is charged with calcium chloride retained in place by means of absorbent cotton plugs. Lump or granulated arsenic-free zinc is introduced into the tube *C*, sulphuric or hydrochloric acid is admitted from the funnel *C* through the cock *g* and tube *E*, followed by the solution to be tested for arsenic after all air has been expelled from the apparatus.

In the application of the Gutzeit, Ritsert, Flückiger, Lohmann[4] methods, applied quantitatively by means of a set of standards for comparison, the drying tube is charged with absorbent cotton and a few strips of lead acetate paper or its equivalent, and the ignition tube is replaced with the curved tube *N*, into which the impregnated test paper is introduced.

The stopper tube *g′* is provided for connection with a supply of arsenic-free hydrogen, as suggested by Munroe and in use by his students,[5] thereby materially reducing the time required for a determination by affording a means of rapidly removing all air from the apparatus, and also effecting a saving of arsenic-free zinc and acid.

Provision is made by the outer vessel or jacket *B*, with the side tubes *b* and *b′*, for either cooling the reaction chamber *C*, as recommended by the earlier authorities, or for heating it as recommended by Harkins,[1] by passing through it either cold or hot water.

---

[1] Edin. Philos., 16, 229.

[2] *Berzelius, Jahresb.*, 17, 191.

[3] *Am. Chem. J.*, 13, 431.

[4] Fresenius, "Qual. Analysis," 3157, 7, e. f.

[5] THIS JOURNAL, 17, 885, 890 (1895).

In the preparation of standard mirrors for comparison, as recommended by Sanger,[2] as small a quantity as 0.005 mg. As_2O_3 may be standardized by means of this apparatus. The mirrors prepared vary distinctly with a variation of 0.005 mg. of As_2O_3 in the known solutions used and duplicate mirrors from equal quantities of As_2O_3 agree quite as well as those illustrated in Sanger's paper.

GEORGE WASHINGTON UNIVERSITY, WASHINGTON, D. C.

A COLORIMETRIC DETERMINATION OF MANGANESE IN THE PRESENCE OF IRON.

BY M. R. SCHMIDT.

Received June 17, 1910.

The following method has been used by the writer for some time, and has been found to give uniform satisfaction in the determination of small quantities of manganese in the presence of iron, in certain pharmaceutical preparations, such as peptonates, sirup of hypophosphites, etc. No originality can be claimed for the method, as it was proposed several years ago by Walter,[3] but it is believed that the details of manipulation here given will lead to the greatest rapidity in attaining accurate results. The usual basic acetate method of separating manganese from iron requires, in order to effect complete separation, at least two precipitations of the iron, and subsequent evaporation of the filtrates in order to insure complete precipitation of the manganese by bromine or other reagents. This involves considerable loss of time, and when dealing with small quantities of manganese, the total experimental errors often amount to a considerable percentage of the weight of the manganese involved. The present method requires no previous removal of iron, and the results are accurate when the total manganese amounts only to a few milligrams. Moreover, duplicate determinations can be made in one-half hour. The determination depends on the power of the persulphates to convert bivalent manganese into permanganic acid in the presence of silver nitrate.

A standard solution of manganese containing 2 mg. of manganese in each 10 cc. is found to be most convenient, and is prepared as follows: Run 182.1 cc. of exactly tenth-normal potassium permanganate solution into a liter flask, add about 100 cc. of 10 per cent. sulphuric acid and 12 cc. of 3 per cent. hydrogen peroxide. Warm the flask slightly until the oxygen is driven off, cool again and dilute to the mark. Prepare also a solution of silver nitrate, containing 20 grams of the salt in a liter. 1 cc. of this solution must be used with each mg. of manganese present.

---

[1] THIS JOURNAL, 32, 520 (1910).

[2] *Loc. cit.*

[3] *Chem. News*, 84, 239 (1901).

To make a determination, remove 5 cc. of the unknown solution to a small beaker by a pipette. Dilute to about 100 cc., add 2 or 3 cc. of ether, and precipitate with ammonium sulphide. Warm the solution on the steam bath, stirring vigorously, and after the precipitate is settled filter through a small folded filter and wash thoroughly with water containing a little ammonium sulphide. Dissolve the precipitate on the filter with the smallest possible quantity of dilute sulphuric acid, collecting the filtrate and washings in a small Erlenmeyer flask. Boil to expel hydrogen sulphide, add a little nitric acid to oxidize the iron and then add one drop of silver nitrate solution. If a turbidity occurs, which indicates imperfect washing of the sulphides, add silver nitrate in very slight excess, boil again, and filter through a small dense filter into a 100 cc. flask. To this solution, which should be perfectly clear, add 1 cc. of silver nitrate solution for each mg. of manganese which is present, followed by about 1 gram of ammonium persulphate, and place the flask on a steam bath. The contents soon turn yellow, then red, and in about one minute the purple color of permanganic acid is fully developed. Cool the flask, fill to the mark, stopper and shake well. Into another 100 cc. flask, introduce 10 cc. of the standard manganese solution, and about 20 cc. of dilute sulphuric acid. Add 2 cc. of the silver nitrate solution and 1 gram of ammonium persulphate, and proceed exactly as with the unknown solution. Fill a burette with the latter, and fill one of two comparison tubes, which must be of the same diameter, with a portion of the standard permanganic acid solution. Fill another burette with distilled water, run about 10 cc. of the unknown solution into the second comparison tube, and dilute with water until the color is equal in intensity to that of the standard solution, viewing the tubes from the side. Suppose, for instance, that 12 cc. of the unknown permanganic acid solution were taken and 18 cc. of water added. This solution, of the same intensity as the standard solution, is of the same strength, and contains 0.02 mg. in 1 cc. or, $(12 + 18) \times 0.02 = 0.60$ mg. in all. This is equivalent to 12 cc. of the original solution, which therefore contains 5 mg. manganese, derived from 5 cc. of the original preparation, giving a percentage of 0.10.

It is found at times that the oxidation of the manganese is only partial, and the solution, instead of becoming purple, is clouded by a brown precipitate of manganese dioxide. In such cases, add a few mg. of sodium sulphite or bisulphite, or a few drops of sulphurous acid solution, until the solution becomes clear again. Then add more silver solution, and another portion of ammonium persulphate and warm again.

The ether used when precipitating the sulphides has the effect of causing the precipitate to settle quite rapidly.

Following are results obtained in duplicate determinations of several preparations. In all of these preparations iron was present in amounts from 3–5 times the amount of manganese.

	1 cc contains milligram Mn.
1	0.205 0.243
2	0.1468 0.1520
3	0.734 0.723
4	0.588 0.606

In order to test the accuracy of the method, 0.6316 gram of crystallized manganous sulphate, free from effloresced portions, was dissolved in 250 cc. of water, 10 cc. of this were taken, and after oxidation diluted to 200 cc.

On comparing with the usual standard, the 200 cc. were found to contain 6.392 mg. of manganese, corresponding to 0.6505 gram of manganous sulphate originally, or 102.9 per cent. To another 10 cc. of the original solution, 1 gram of iron alum was added and the manganese determined as before. In this case 6 178 mg. of manganese were indicated in the 10 cc., corresponding to 99.2 per cent. of theory. Here the concentration of the iron was roughly 20 times that of the manganese.

The method has already been applied to the determination of manganese in rocks,[1] and should prove excellent for determining manganese in waters.

LABORATORY OF SHARP & DOHME.

NOTES.

The Chemical Laboratory of the University of Washington.—The University of Washington on April 16, 1910, formally opened for use a new chemical laboratory which cost when completed a total of $230,000. This building is of concrete and steel construction and is three stories in height. The design of the building was made by the architects of the Alaska-Yukon-Pacific Exposition according to drafts prepared by the writer after his visit to all the modern laboratories of Europe and America. It contains certain features of construction which may be of interest to those chemists who are contemplating erection of buildings or equipment of laboratories. A drawing of the general floor plan of the building accompanies this note.

---

[1] Hillebrand, *Bull.* 305, U. S. G. S., p. 99 (1907).

It will be observed that the offices and classrooms occupy the central portions of the building and the laboratories the outlying wings. The main laboratories, 12 in number, are separated by a line of flues extending from the basement to a tunnel immediately beneath the roof. These two lines of flues are exhausted by large fans run with a common motor. It will be seen also that this plan involves the use of light from only one end and side of each laboratory, the hoods occupying the one long side of each laboratory. This plan would have been attempted with some hesitancy had it not been for the unqualified satisfaction expressed by Professor Witt in Charlottenberg with the side lighted laboratories. It is with considerable satisfaction that we find the result of this construction is an eminently satisfactory lighting and ventilating system—both work admirably.

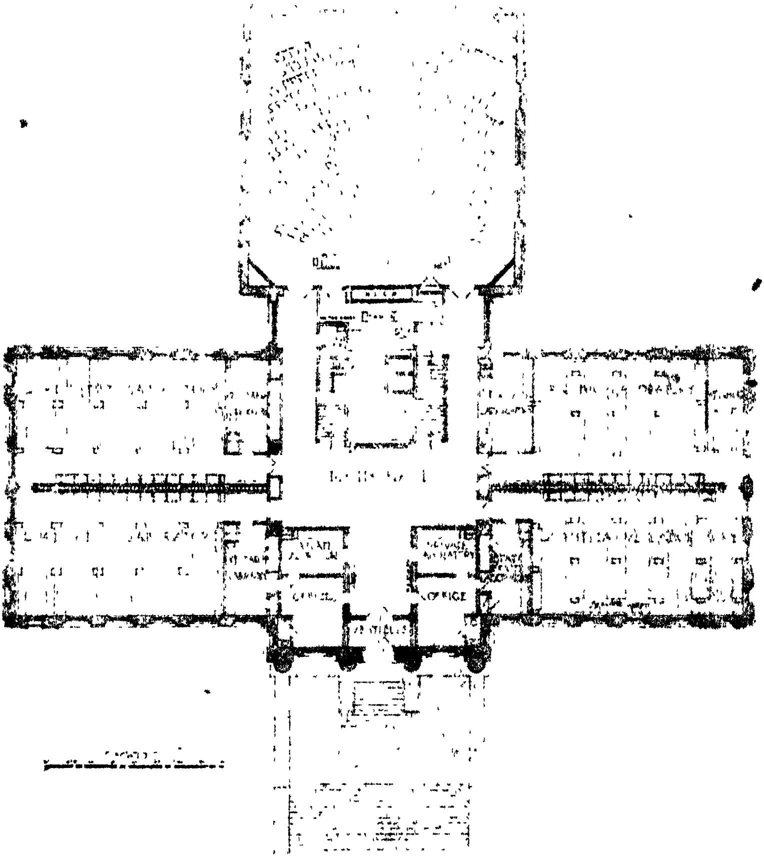
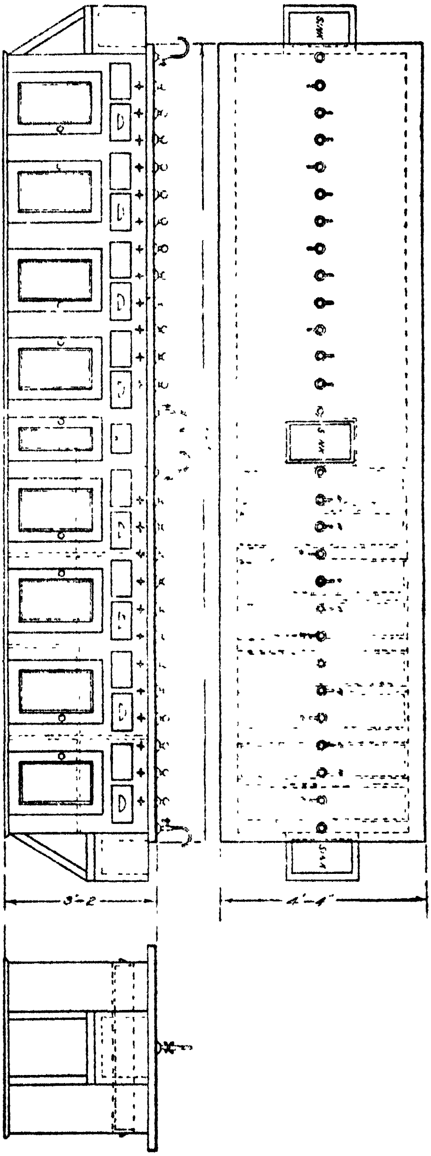


Fig. 1.

A second feature of the laboratory is the use of alberene stone, exclusively, for sinks and for the floors of the hoods. Only two types of desks were provided for the laboratory. These desks are primarily, for general chemistry, type 1; and quantitative work, type 2. It is type 2 which varies most from the common laboratory construction and which has proven the most satisfactory. This is illustrated in Fig. 2. All stopcocks are operated by a long arm control situated immediately beneath



QUANTITATIVE ANALYSIS DESK
UNIVERSITY OF WASHINGTON

Fig. 2.

the ledge of the desks. No obstruction is therefore placed upon the tables except the gas and water outlets. The table tops are finished with the aniline black finish recommended by the United States Bureau of Chemistry. The table tops are of Washington fir and similar tables have been in use in this university for six years without needing either refinishing or repairing.

The pressure system and the hydrogen-sulphide system reach the hoods only, which also are furnished with gas and water. The hydrogen-sulphide generating apparatus is situated without the building on the roof. It is of the general type used by Professor Fischer, of the University of Berlin, and is not wholly satisfactory. The air-pressure system is automatic and varies between 45 and 15 pounds in the compressor, being delivered into the laboratory at a uniform pressure of 15 pounds. We find this most satisfactory for blast lamps.

One item of construction has proven highly satisfactory. The main lecture room, as shown in Fig. 1, opens directly into the stockroom, the rear half of which is equipped as a preparation room for the lecture. Back of the lecture table is a hood slightly raised above the level of the table, opening both into the stockroom and lecture room, and ventilated by a separate one-horse power motor. This makes the disposition of ill-smelling or poisonous materials extremely easy and effective. The lecture table is practically an exact duplicate of that of Professor Beckmann of the University of Leipsic.

The stock rooms occupy a tier of three rooms, one on each floor, in the exact center of the building and are connected both by an elevator and an internal stairway. An excellent feature is a large room 40 by 60 feet with concrete floor covered with asphalt and brick walls and concrete pillars, which is for the machinery used in the laboratory, such as grinding machines, filter presses, cement testing material, stills, etc.; in general those operations which are carried out on a large scale and are likely to be either dirty or dangerous.

The main hall in two floors of the building is equipped with a very complete "first aid to the injured" set of materials. These cases are always open and have on them simple directions for emergency surgery. These have already shown their great value as time and trouble savers as well as guaranteeing a certain immunity from serious injury.

The department is also equipped with a departmental library, which promises to be eminently satisfactory.

We have made certain mistakes in the construction of the laboratory, of course, and were limited financially and so prevented from putting in certain desirable features, for example, an exhaust system for filtration. Taken all in all, however, the laboratory is a source of great satisfaction and considerable pride on the part of the writer and he will be glad to do whatever he can in assisting others to profit both by our successes and failures.

H. G. BYERS.

A Modified Burette for Standard Alkali Solutions. Glass stoppered burettes offer serious obstacles to their constant employment for standard solutions of caustic alkalis. The tendency of the stopcock to stick, rapid wear, resulting in leakage, or breaking of the cock or of the shell, and other difficulties constitute serious objections to this form of burette for caustic alkali solutions. The type of burette in which a glass tip is connected to the burette by means of a rubber tube, the flow being controlled by a pinchcock or a glass ball, is an alternative which is still in considerable use, but the objection to this type on the ground of inaccuracy is well understood, and the United States Bureau of Standards will not calibrate such burettes.

It occurred to the writer that the substitution of metal for glass for the movable part of the stopcock might overcome the difficulty and that of the metals adapted to this purpose, silver might perhaps be preferable both because of its fairly good resisting powers towards caustic alkali, as well as on the ground of reasonable cost. Accordingly, a burette fitted with a silver stopcock was tried by filling with half-normal potassium hydroxide solution and allowing to stand for a week. The stopcock did not show the slightest sign of sticking or leakage. The burette was then emptied and filled with 30 per cent. sodium hydroxide solution and in the course of several weeks the stopcock was operated several times nearly every day. The stopcock is still apparently in as good condition as when first received, although it has not been lubricated again since it was first put into use. This stopcock was made for the writer by the Bausch & Lomb Optical Company, of Rochester, New York.

PAUL RUDNICK.

CHEMICAL LABORATORY OF ARMOUR AND COMPANY,
CHICAGO, ILL.

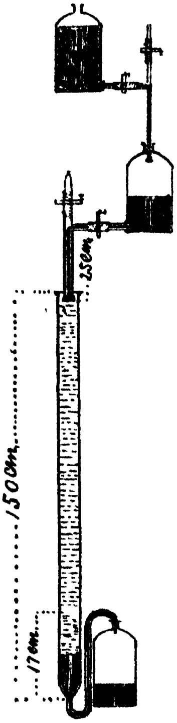
The Purification of Mercury.—The accompanying cut is of an apparatus which has been used by the writer in the Harvard laboratory for more than a year, and he believes it possesses several advantages over the original apparatus of L. Meyer,[1] and, perhaps, over a somewhat similar modification of the original by Hildebrand[2] in that large quantities of mercury can be rapidly and thoroughly freed from those substances which are likely to occur in it and which dissolve in dilute nitric acid or in mercurous nitrate.

The method of Meyer is so familiar to every one that details are unnecessary. The writer uses a 5 cm. tube, 1.5 m. long. He finds that 8 per

---

[1] *Z. anal. Chem.*, 2, 241.

[2] THIS JOURNAL, 31, 933.



cent. acid is better than the more dilute solution recommended by Meyer.

The mercury is atomized by forcing it through chamois skin tightly stretched over the end of a 25 mm. tube and bound fast by means of a cord. This large tube is drawn down sharply as shown in the figure and sealed to a 5 mm. tube which is attached to the T-tube of the aspirator bottle. It is so adjusted that the atomizing skin is about 15 mm. above the surface of the acid, and the pressure of the mercury is so regulated by means of the screw pinchcock as to make the fine streams just continuous, otherwise the skin may be so distended as to become hemispherical, in which event some of the mercury may be sprayed on the sides of the tube and collect in small drops.

The object of the upper aspirator bottle and filter, precisely like the lower one, is to increase the capacity of the reservoir and to remove solid particles which tend to clog the pores of the atomizing skin.

In offering the above suggestion the writer lays little claim to originality. It is but a slight modification of a time-honored method, but he does claim that in his hands it works far more rapidly, requires no attention, and the product obtained by one passage through the acid is much purer than by the original method, and he trusts that others may have a like experience with it.

C. J. MOORE.

CAMBRIDGE, MASS

On the Preparation of a Cuprous Nitrate, $CuNO_3.2NH_3$.—Cuprous nitrate, of the formula $CuNO_3.2NH_3$, was prepared as follows:

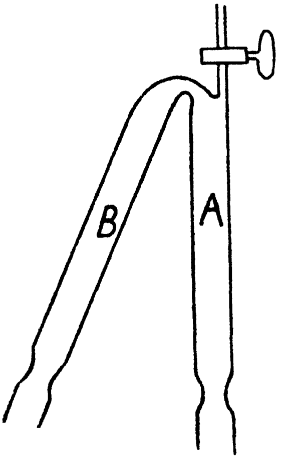
A glass tube of two arms, the one carrying a stopcock, was drawn out as shown in Fig. 1. An approximately weighed amount of dried cupric nitrate of the formula $Cu(NO_3)_2.4NH_3$[1] was introduced into the arm A and the stopcock attached to a cylinder of dried ammonia. Ammonia was then passed through both arms and A sealed off. A piece of bright copper foil was then introduced into B and the arm sealed off at the lower end.

Ammonia was now distilled into A under pressure (A was placed in ice water for this purpose) until nearly full. The solution of cupric nitrate was then poured over into B. A was washed free of cupric nitrate by distilling some ammonia over from B, and then pouring it back again. This was repeated until no color was obtained in A. The solution was then allowed to stand in contact with the copper foil until the color of deep blue gave way to a practically colorless solution.

---

[1] $Cu(NO_3)_2.NH_3$ is easily prepared by supersaturating an aqueous cupric nitrate solution with ammonia, when it crystallizes out, and may then be washed and dried over sulphuric acid. It is a stable salt in contact with the air, and is very soluble in ammonia

The solution was then transferred to A, and B washed by repeated distillations of the ammonia from A to B, and then pouring back into A. The ammonia was then allowed to gradually distil off through the stopcock. As the solution concentrated, the cuprous nitrate crystallized out. A was then sealed off, evacuated, and weighed. The salt was then dissolved in dilute nitric acid, washed out, and the copper determined electrolytically. The tube was dried, evacuated and weighed.



The weight of the crystallized salt was 0.5786 gram; weight of copper 0.2292 gram, giving 39.61 per cent. copper, in fair agreement with the formula $CuNO_3.2NH_3$ which requires + 39.86 per cent. The increased weight of salt obtained corresponds (weighings of cupric nitrate and copper foil approximate) to the loss of weight in the copper foil.

The salts obtained were not entirely pure. A few blue crystals separated out with the colorless cuprous nitrate, showing the presence of a little cupric nitrate. This could not be separated owing to their similar solubility. Possibly this could be avoided by using more elaborate apparatus, but it seemed as if there was a point of equilibrium reached when the cupric nitrate was nearly reduced. The salt is not stable in the air, oxidizing very rapidly.

A recent analysis of another sample by Mr. G. H. Bohart, of this laboratory, in which the nitrogen was also determined, gave practically the same result for the copper content, and also agreed very closely with the theoretical nitrogen content for the above formula.

The preparation of the above salt was suggested by Prof. E. C. Franklin.

W. H. Sloan.

[Contribution from the Chemical Laboratory of the Massachusetts Institute of Tech.]

THE CONDENSATION OF SOME PRIMARY AROMATIC AMINES WITH CHLORAL-ANILINE.

By Stroud Jordan.

Received June 10, 1910

It has been known for a long time that when one molecule of an amine, as aniline, is brought in contact with one molecule of an aldehyde, as chloral, an addition product will be formed, but if the amine is increased to two molecules while the aldehyde is kept constant at one molecule a condensation product will be formed and a molecule of water will be eliminated.[1] Further than this, no definite relationship has been established between these two reactions, so that the purpose of this paper will be to point out some of the relations existing between these two reactions and their products.

It has been shown in the following work that it is possible to form a condensation product by the action of one molecule of a free amine with one molecule of an addition product, without the presence of free chloral. It has also been shown that it is possible to form a condensation product in which two unlike amines will be joined to the same chloral residue, by the action of one molecule of a free amine with the addition product of chloral and an unlike amine. By these two experiments it has been shown that the addition product *can* be an intermediate step in the formation of the condensation product and that it will change over into the condensation product upon the addition of an excess of a free amine.

The products which will be studied in the following work are:

First, the condensation of aniline with chloral-aniline, and

Second, the condensation of 1,3,4-nitrotoluidine with chloral-aniline. In this second product it will be noticed that it was very difficult to prepare a pure sample of the condensation product, on account of the ease with which it decomposed in nearly every solvent. This decomposition product was proved to be 5-chlorine-3-nitro-4-toluidine and this work will be taken up later, in this laboratory, as a probable method of chlorination for the aromatic amines. This work will also be followed up later to determine the rate of reaction and also as a study of intermediate reactions.

Experimental.

The Condensation of Aniline with Chloral-aniline.—For this preparation eight grams of the freshly prepared addition product were dissolved in one hundred cc. of 95 per cent. alcohol and to this were added three grams of pure aniline after which the whole mass was heated up to boiling and then allowed to stand for six hours. This gave a light yellow solution which crystallized out, on evaporation over a water bath. This crude compound consists of yellowish crystal masses which melted at 98–100°, but after two crystallizations from alcohol and petroleum ether it gave pure, white needles, melting at 107–8°. This compound was proved to be the condensation product, by making its hydrochloride and hydrobromide, by the melting point of the aceto derivative, by its crystalline form and melting point and by the detection of free aniline and chloral, when the condensation product was decomposed.

From the above reactions it may be concluded that the condensation of aniline and chloral may be made by the interaction of one molecule of aniline with one molecule of chloral-aniline, thus dividing the condensation reaction into two steps: $C_6H_5NH_2 + CCl_3CHO = C_6H_5NH—CCl_3CHOH$, and $C_6H_5NH—CCl_3CHOH + C_6H_5NH_2 = (C_6H_5NH)_2CCl_3CH + H_2O$.

The Condensation of 1,3,4-Nitrotoluidine with Chloral-aniline.—For this preparation one and one-half grams of aniline and two and one-half grams of chloral were brought together in an open vessel, without the presence of a solvent. The temperature was never allowed to exceed 40° so that no water would be driven out from the reaction, thus guarding against the formation of any condensation product. This reaction gave the addition product of aniline and chloral, described by A. Eibner.[1] To this addition product were added two and six-tenths grams of 1,3,4-nitrotoluidine, which had been previously dissolved in one hundred cc. of benzene, after which the whole mass was heated at a slow boiling temperature for two and one-half hours, under a reflux condenser. This solution was then filtered off from any byproduct that might be present and the clear benzene solution was allowed to crystallize out, which gave a yield of six and two-tenths grams of a crude product melting at 90–6°, being approximately a 95 per cent. yield of the theoretical amount of condensation product which should have been formed by this reaction. The crude product, obtained in this manner, was purified by crystallization from benzene at room temperature, raising the melting point to 98–9°. This compound crystallized from benzene in light, yellowish-brown, crystal masses which crawled up the sides of the beaker. It was easily soluble in alcohol, acetic acid, acetone, benzene, ether and toluene, but not so soluble in gasoline, petroleum ether and ligroin.

Three analyses of this compound, for chlorine, gave: 28.44, 27.45 and 28.07 per cent. Cl, calculated for $C_{15}H_{14}N_3O_2Cl_3$, 2840 per cent.

This condensation product was apparently unaffected when treated with water, either hot or cold, for only a slight amount of decomposition was ever noticed, but when it was treated with concentrated hydrochloric acid a mixture of aniline hydrochloride, nitrotoluidine hydrochloride and free chloral was obtained. These compounds were recognized by making the hydrochloric acid solution alkaline with sodium hydroxide and distilling with steam. The aniline came over in the first distillate, mixed with a little nitrotoluidine, while the nitrotoluidine remained behind in the distilling flask, mixed with a little aniline. These two compounds were proved to be present by their behavior with acids, melting points and other derivatives. The toluidine gave a melting point of 78° and formed a hydrochloride which decomposed at 230–4°, while the aniline gave the characteristic phenyl isocyanide odor and an acid derivative with hydrochloric acid, which was proved to be the hydrochloride of aniline.

---

[1] *Ann.*, 302, 340–80 (1898).

When bromine was added to a glacial acetic acid solution of the condensation product it reacted very vigorously, forming a white, crystalline precipitate and liberating chloral. This bromine derivative was proved to be a mixture of the aniline and nitrotoluidine hydrobromides and some of the higher bromine derivatives, by making it alkaline with sodium hydroxide and distilling with steam. Free aniline was the first to come over with the steam and was recognized by making its hydrochloride and acetyl derivative. The nitrotoluidine remained behind in the distillation flask and was recognized by its melting point and the decomposition point of its hydrochloride. The separation of these two amines was not complete, for there was always a trace of the nitrotoluidine in the aniline distillate and the residue, left in the distillation flask, was mixed with some of the higher bromine derivatives and some free aniline.

A molecular weight determination was next made, using glacial acetic acid as a solvent, but there was always an error, due to the fact that the condensation product was unstable and would break down into 5-chlorine-3-nitro-4-toluidine. While this decomposition was very slight, it was sufficient to keep the molecular weight low and the best result that was obtained, by the freezing point method, was 348.+. The theoretical molecular weight for this compound should be 374.+. This molecular weight will show, however, which of the three following possibilities this compound really is:

Substance	M P	M W	Per cent. Cl.	Color.	Form.
The condensation of aniline and chloral..	107–8°	315.35	33.72	White	Needles
The condensation of nitrotoluidine and chloral......	108–9°	433.35	24.52	Golden yellow	Needles
	Found.	Found.	Found.	Found.	
The condensation of aniline, chloral and nitrotoluidine..	98–9°	348	28.44	Yellowish	Masses
		Theoret.	Theoret.		
		374.35	28.40		

In considering the two possibilities with which the mixed-type condensation has been compared it has been assumed that when the nitrotoluidine is added to the addition product of aniline and chloral either a mixed-type condensation has been formed or a reaction has taken place causing the addition product to change over into a simple condensation product with the liberation of half of the chloral and one molecule of a free amine, either aniline or nitrotoluidine. No mention has been made of the possibility of a mixture which would contain the condensations of aniline and chloral and nitrotoluidine and chloral because the crude products, and also the purified products, which have been obtained by this work, have always shown very constant melting points and the behavior towards acids has always been the same.

From the foregoing work it has, therefore, been concluded that the mixed-type condensation product has been prepared in which one molecule of aniline and one molecule of nitrotoluidine are condensed with one molecule of chloral, according to the following reactions: $CCl_3CHO + C_6H_5NH_2 = CCl_3CHOH\ NHC_6H_5$, and $CCl_3CHOH\ NHC_6H_5 + C_7H_5N_2O_2 = C_{15}H_{14}N_3O_2Cl_3 + H_2O$.

The subsequent decomposition of this condensation product, giving 5-chlorine-3-nitro-4-toluidine, would probably take place in the following two steps, for the reason that nitrotoluidine and chloral will form an addition product which breaks down into the same chloral derivative, without the presence of either free or combined aniline: $C_{15}H_{14}N_3O_2Cl_3 \longrightarrow CCl_3CHOH.NHC_6H_3NO_2CH_3 + C_6H_5NH_2$, and $CCl_3CHOH.NHC_6H_3NO_2CH_3 + HCl \longrightarrow C_7H_8N_2O_2Cl$ + aldehyde derivative.

BOSTON, MASS

THE DETERMINATION OF TOTAL SULPHUR IN ORGANIC MATTER.

BY HERMAN SCHREIBER

Received June 7, 1910.

Introduction.

A great many methods have been proposed for the determination of total sulphur in organic matter, but probably only two of these are either easy to manipulate or accurate, namely, the Barlow-Tollen,[1] or absolute method, and the Osborne,[2] or peroxide method. When the latter is applied to solid material, however, it leaves much to be desired in the way of ease of manipulation and speed, and has absolutely no claim to exactness of detail. It is true that the water used for moistening the sample is measured and the sodium carbonate is weighed, but the amount of sodium peroxide added varies with the material analyzed and with the rate at which the reagent is added. The amount of acid which must be added after fusion is also an unknown factor; it varies in each case which necessitates making the solution alkaline again, and then acid. These, however, are not all of the difficulties encountered. The fusions have a tendency to burn and blow out of the crucible, and this happens most frequently when the determinations must be rapidly made, for the peroxide method has a dignity all its own and will brook no haste or impatience. All of these objections were keenly realized when it became necessary to make about 100 sulphur determinations in a recent research.

---

[1] THIS JOURNAL, **26**, 341 (1904).

[2] U. S. Dept. Agr., Bureau of Chemistry *Bull.* **107**, revised, p. 23.

An ideal method for this determination should embody several features: First, it must not call for excessive amounts of reagents, nor such as will interfere with the precipitation of the barium sulphate or contaminate the precipitate; second, the reagents employed must serve two purposes, they must destroy all of the organic matter and all of the sulphur must be fixed and oxidized to sulphate; third, the method must be fairly rapid and not require a large amount of practice, so that an analyst can make the determination from time to time without great delay and difficulty.

It is difficult to outline a method which will meet all of these conditions, but after making quite a number of experiments the following procedure was evolved, which seems to fulfil the requirements more nearly than the peroxide method.

The Proposed Method.

Weigh 1 gram of material in a nickel crucible of 100 cc. capacity, add 10 cc. of a solution made by dissolving 100 grams of sodium nitrate and 150 grams of sodium hydroxide in 500 cc. of water. Then add 5 grams of crystallized magnesium nitrate and stir with a platinum rod, making sure that the mass is thoroughly mixed and that the sample is broken up as much as possible. Wash down the material adhering to the stirring rod and sides of the crucible with the smallest possible amount of water. (This is essential since the addition of much water will prolong the subsequent heating unnecessarily.) Heat for one hour on a hot plate covered with a thin sheet of asbestos paper, keeping the temperature at about 130°. Then put the cover on the crucible, tilting it in such a fashion as to leave an opening for the steam to escape and heat further for one hour at from 150–160°, or until the material is entirely dry. If the fusions begin to bump, lower the heat so that the covers will not be jarred down tight on the crucibles, and the material lost by frothing. When the mass is entirely dry, put the covers on tight and heat gradually until the temperature reaches 180°, then heat for thirty-five minutes, maintaining the temperature at about 180–200°. These temperatures were determined by laying the thermometer down on the hot plate.

Now set the crucible (with the cover on tight) into a round hole in a piece of asbestos board, so that about 1.5 inches of the lower part of the crucible shall project below the asbestos board as Lunge[1] has directed, the asbestos board to be laid flat. Heat with the Bunsen burner for half an hour, allowing the flame to just touch the bottom of the crucible during the first fifteen minutes, and then with the full heat during the last fifteen minutes. (Never let the inner cone of the Bunsen burner strike the crucible.) During the first five minutes of heating with the full flame keep the crucible in an upright position, then remove the cover and tilt the crucible so as to fuse any material which may have crept up the sides. Then return the crucible to the upright position, replace the cover, and heat for five minutes more. When the fusion has solidified, and before it has entirely cooled, place the crucible in a 600 cc. beaker with 150 cc. of distilled water and cover with a watch glass. Put the crucible cover in the beaker, beside the crucible, and slightly rotate and tilt the beaker so that all parts of the crucible shall be touched by the water. Run in 13 cc. of hydrochloric acid (specific gravity 1.19) from a burette and again rotate the beaker slightly. Tip the crucible so that the other side comes in contact with the acid liquor, allow it to stand a few minutes, and remove the crucible and cover, washing the liquid adhering to them back into the beaker by means of distilled water. Any fused material adhering to the sides of the crucible can easily be removed with a stirring rod. Place the beaker on the steam bath and heat for about half an hour and then let it stand in the cold over night. Filter and wash the insoluble residue. Heat the filtrate on the steam bath or otherwise, and precipitate with a 10 per cent. barium chloride solution.

---

[1] *Chemisch-Technische Untersuchungs Methoden*, 1, 428 (1904).

In all of the determinations here reported the solutions were precipitated by heating on the steam bath, adding 10 cc. of barium chloride to the solution quickly, and stirring as soon as the precipitate began to form. After adding the barium chloride the solutions were allowed to remain on the steam bath about one hour, and were then removed to the table and stood in the cold over night, after replacing any water lost by evaporation. All filtrations, except the solution of the fusions of the barium sulphate with sodium carbonate, were filtered through S and S blue ribbon filter paper. The fusions of the barium sulphate were filtered through white ribbon filter paper and all precipitates were washed with cold water.

In this method a crucible loses from 0.3–1.3 grams of its weight in each determination, an average of 0.9 gram as calculated from 20 determinations. By the peroxide method the crucible loses from 1.2–2 grams of its weight in a fusion, an average of 1.4 grams based on 13 determinations. Using a griddle hot-plate, 14 by 18 inches, 18 fusions can easily be made in a day. The only way in which a determination can be lost is by heating too rapidly on the hot-plate, thus causing it to boil over or spatter.

Description of Samples and Analytical Results.

Total sulphur was determined by both the peroxide method and the proposed method on five samples of dried white of eggs, three of which were made from the same lot of eggs by boiling with various amounts of copper sulphate, washing free of copper, and drying and grinding; one was a sample of commercial dried albumin; and one was the white of eggs

TABLE I.—COMPARISON OF THE RESULTS BY THE PEROXIDE AND BY THE PROPOSED METHOD FOR THE DETERMINATION OF TOTAL SULPHUR.

			Peroxide method [1]					Proposed method [1]				Peroxide method averages		Proposed method averages.		
			First precipitation.		Reprecipitation [2]			First precipitation		Reprecipitation [2]						
Number of sample.	Description of sample	Amount of sample. Grams	Grams of sulphur.	Per cent. of sulphur.	Grams of sulphur	Per cent of sulphur.	Amount of sample Grams	Grams of sulphur.	Per cent. of sulphur.	Grams of sulphur.	Per cent of sulphur.	A. Before fusion Per cent	B. After fusion Per cent.	C. Before fusion. Per cent	D After fusion. Per cent.	Difference between columns B and C. (B-C.) Per cent.
1	White of egg	1.0035	0.0162	1.61	.	.	1.0045	0.0151	1.50	.		1.64		1.54	.	.
		0.9955	0.0166	1.67	.	.	1.0025	0.0159	1.58							
2	White of egg.	0.9978	0.0167	1.67	..	..	1.0015	0.0145	1.45	..	..	1.67	..	1.49		..
		1.0025	0.0167	1.67	..	..	0.9995	0.0153	1.53	..	..					
3	White of egg	1.0148	0.0163	1.61	..	..	1.0100	0.0160	1.58	.	..	1.64	..	1.58		..
		1.0330	0.0172	1.67	..	..	1.0075	0.0158	1.57	..	.					
51	White of egg.	1.0110	0.0153	1.51	..	..	1.0055	0.0139	1.38	..	.	1.49	.	1.35		
		1.0035	0.0146	1.46	.	..	1.0160	0.0133	1.31	..	.					
54	White of egg.	1.0046	0.0131	1.30	..	..	1.0045	0.0133	1.32	..	..	1.35	..	1.29		.
		1.0000	0.0138	1.38	..	..	1.0023	0.0125	1.25	..	..					
	Blank	....	0.0017	..	..	..	..	0.0004	..	..	..	..	..	..	..	..
A	Mustard (ground).....	1.0015	0.0124	1.24	0.0122	1.22	1.0105	0.0120	1.19	0.0111	1.10	1.24	1.22	1.19	1.10	+0.03
		1.0030	0.0124	1.24	0.0122	1.22	1.0035	0.0119	1.19	0.0111	1.10					
B	Mustard (ground).....	1.0040	0.0130	1.30	0.0128	1.28	1.0050	0.0146	1.45	0.0124	1.23	1.28	1.28	1.32	1.22	—0.04
		1.0255	0.0128	1.25	0.0130	1.27	1.0050	0.0118	1.18	0.0121	1.20					
C	Mustard (ground).....	1.0025	0.0128	1.28	0.0120	1.20	1.0040	0.0120	1.20	0.0111	1.10	1.26	1.22	1.21	1.10	+0.01
		1.0075	0.0124	1.23	0.0124	1.23	1.0213	0.0125	1.22	Lost	..					

D	Mustard (ground).....	1.0135	0.0158	1.56	0.0157	1.55	1.0120	0.0133	1.32	0.0137	1.35	1.52	1.51	1.40	1.37	+0.11
		1.0000	0.0147	1.47	0.0146	1.46	1.0060	0.0148	1.47	0.0139	1.38					
E	Mustard (ground)....	1.0080	0.0142	1.41	0.0140	1.39	1.0017	0.0133	1.33	0.0124	1.24	1.35	1.34	1.32	1.17	+0.02
		1.0035	0.0129	1.29	0.0128	1.28	1.0000	0.0131	1.31	0.0109	1.09					
	Blank...............	..	0.0009	..	0.0011	..	.	0.0004	..	0.0007	.	.	.		.	..
7931	Valve rubber.........	1.0000	0.0435	4.35	0.0426	4.26	1.0135	0.0435	4.29	0.0417	4.12	4.35	4.27	4.27	4.10	±0.00
		1.0155	0.0441	4.34	0.0432	4.27	0.9990	0.0425	4.25	0.0407	4.07					
7934	Valve rubber.........	1.0000	0.0438	4.38	0.0430	4.30	1.0075	0.0415	4.12	0.0397	3.94	4.35	4.20	4.21	3.95	+0.05
		1.0025	0.0432	4.31	0.0422	4.21	1.0055	0.0432	4.30	0.0397	3.95					
7935	Valve rubber.........	1.0045	0.0324	3.23	0.0305	3.04	1.0045	0.0286	2.85	0.0276	2.75	3.19	2.92	2.88	2.77	+0.04
		1.0040	0.0316	3.15	0.0281	2.80	1.0075	0.0292	2.90	0.0281	2.79					
7937	Valve rubber.........	0.9990	0.0435	4.35	0.0428	4.28	1.0055	0.0417	4.15	0.0401	3.99	4.30	4.21	4.14	3.99	+0.07
		1.0010	0.0425	4.25	0.0414	4.14	1.0035	0.0413	4.12	0.0400	3.99					
8136	Tubing.............	1.0040	0.0846	8.43	..	..	1.0230	0.0805	7.87	0.0771	7.54	8.44	8.38	7.82	7.50	.
		1.0080	0.0852	8.45	..	..	1.0660	0.0827	7.76	0.0794	7.45					
		..	..	..	..	..	1.0035	0.0798	7.95	..	..	..	..	8.20	..	..
		..	..	..	..	..	1.0135	0.0820	8.09	..	..					
	Tubing[3]...	..	..	8.12	..	..	..	..	..	0.0000	..	8.06	..	..	..	..
		..	..	8.00	..	..	..	..	..	..	..					
	Blank...............	..	0.0022	..	0.0028	..	..	0.0002	..	0.0000	....	..	..	..	..	..

[1] Results given have been corrected for blank.

[2] After fusing barium sulphate with sodium carbonate.

[3] Determination by E. W. Boughton, Contracts Laboratory.

boiled in the shell, dried, and ground. Sulphur was also determined on four samples of mustard seed, and one sample of ground mustard. *A* is pure white mustard, *B* is black mustard containing 64 per cent. of charlock, *C* is commercial ground mustard, *D* is pure brown mustard, and *E* is commercial ground seed. These samples were furnished by the Microchemical Laboratory. Sulphur was also determined on five samples of vulcanized rubber furnished by the Contracts Laboratory.

The 60 determinations were made without repeating any, except No. 8136, unless a loss occurred by the leaking of the crucible. This happened in three instances only, so that the work represents fairly well the results which the two methods will give under the same conditions without repetition and selection of results. Twelve determinations were made at a time with each kind of material, two determinations on each sample, and two blanks. The results obtained are given in Table 1. The peroxide fusions were not hurried, but were allowed to fuse for three or four hours. No. 8136 is a sample of rubber tubing which was not ground very finely, and which had been found to contain about 50 per cent. of free sulphur. These facts probably account for the discrepancies in the determination.

Discussion of Results.

Skinner[1] comparing the Barlow-Tollen's and peroxide methods found that the latter gave slightly higher results in five out of seven cases, the difference averaging about +0.11 per cent. of SO_4 or +0.036 per cent. of sulphur. The proposed method gives sulphur results about 0.1 per cent. lower than the peroxide method, the average of the 12 values which were lower by the proposed method would thus be about 0.064 per cent. less than by the absolute method. Both of these discrepancies are well within the experimental error. Also it should be noted that the difference between the figures obtained by fusing the barium sulphate in the peroxide method and reprecipitating, and those resulting from the first precipitation by the proposed method (as given in columns B and C, Table 1) varies from —0.04 to +0.11 per cent. In six out of twelve cases the figures obtained by the first precipitation in the proposed method are nearer the values obtained by fusing and reprecipitating the barium sulphate in the peroxide method than they are to the results of the first precipitation in the peroxide method. The peroxide method gives a very high blank as compared to the proposed method; with the former this blank amounted to from 0.009–0.0028 per cent. of sulphur and in the latter it amounts to from 0–0.0007 per cent. As the blanks by the peroxide method are very high an error would be introduced if they were not run in each set. This is very clearly demonstrated in the determinations of sulphur in sulphuric acid solutions as given in Table 2.

---

[1] U. S. Dept. Agr., Bureau of Chemistry, *Bull.* 116, p. 92.

Sulphuric Acid Solutions.

To determine the effect of the salts in solution on the precipitation of sulphuric acid, fusions were made by the peroxide method and by the proposed method, definite volumes of dilute sulphuric acid being added to the solutions and blanks run at the same time. The fusions were made exactly as in the case of the total sulphur determinations given in Table 1. Then they were dissolved, an excess of 2 cc. of hydrochloric acid was added, the solution was filtered, and the measured amount of dilute sulphuric acid added. The sulphuric acid was precipitated with barium chloride solution in the same manner as in the other determinations. The results are given in Table 2.

TABLE 2.—DETERMINATION OF SULPHUR IN DILUTE SULPHURIC ACID SOLUTIONS BY FOUR DIFFERENT METHODS.

Quantity of solution used cc	By precipitating from distilled water after adding 2 cc excess of concentrated hydrochloric acid Gram.	By weighing as ammonium sulphate by Lunge's method Gram	By precipitating from a solution containing a fusion.	
			By the proposed method. Gram	By the peroxide method. Gram.
10 of solution A . . .	0.0140	0.0142	0.0141	0.0127
	0.0141	0.0142	0.0141	0.0147
25 of solution A	0.0352	0.0350	0.0362	0.0340
	0.0351	0.0349	0.0361	0.0355
10 of solution B . .	0.0799	0.0795	0.0832	0.0811
	0.0800	0.0796	0.0832	0.0805
Blanks[1]	. .	.	0.0001	0.0024

The proposed method gives results 0.1 per cent. too high when 3.5 per cent. of sulphur is in solution and 0.3 per cent. too high when 8 per cent. of sulphur is present. This occlusion of salts evidently compensates for an error which would cause the result to be low, as can be seen from Table 1 and the experimental data.

Lunge and Stierling[2] found that in the precipitations of sulphuric acid in aqueous solution and in the presence of salts, the quick addition of the barium chloride solution gave erroneous data in aqueous solution and correct results in the presence of salts while the slow addition of the precipitant gave just the opposite.

The proposed method employs about 7.6 grams of salt (calculated as chlorides) and the peroxide method 15 grams or more.

[1] Corrected for in values given.

[2] See also Allen and Johnston, THIS JOURNAL, 32, 617, where they state, "A very good uncorrected determination may be obtained by precipitating rapidly but it is due to partial compensation of variable errors, and is not in any case so reliable as one which is made by slow precipitation and corrected as described." This agrees with Lunge and Stierling's conclusion on page 350 of their article, 6th Intern. Congress Applied Chem., 1906, p. 347.

Preliminary Experiments.

The preliminary experimental work leading up to this method consisted in testing the various reagents which have been proposed in methods for the determination of sulphur, varying the temperature, reagents, and time and manner of treatment. The 22 experiments made involved 160 single determinations exclusive of those that were lost on account of faulty manipulation, or seemed valueless from the nature of the reaction.

Determinations were made by using mixtures of reagents composed of from 1.25–3 grams of sodium hydroxide, 5–15 cc. of water, 0.5–1 gram of sodium carbonate, 1–2 grams of sodium nitrate, 1–3 grams of magnesium oxide, and from 3–10 grams of crystallized magnesium nitrite.

The treatment of the material with the reagents varied from drying on the steam bath and burning to heating at from 80–230° for from one and a half to five hours before burning. By these means values were obtained which ranged, for instance, from 1.13–1.45 per cent. of sulphur on a sample which contained 1.56 per cent. by the peroxide method, and from 3.91–4.50 per cent. on a rubber containing 4.17 per cent. by the peroxide method. Of 75 determinations, each the average of two duplicates, the peroxide value was the highest except in three instances. When the preliminary heating was continued for from two and a half to five hours, rising above 175° for at least thirty minutes of that time, it was noticed that the values usually approached the peroxide value by 0.1 per cent.

These preliminary determinations all indicate that adding reagents in solution, drying, and then ashing causes a loss of sulphur and that the substance must receive a definite preliminary heating before the sulphur can be absorbed by the alkaline reagent. This was noted after repeated experiments had been made with modifications of Eschka's method and it seemed probable that when the alkaline reagent was added in solution, the mixture dried down, and a coating consisting of an alkaline oxidizing medium was formed, all of the sulphur would be absorbed. This idea was substantiated by subsequent experiments.

Potassium salts were not tried in any of the experiments as Lunge and Stierling[1] have found that potassium chloride dissolves twice as much barium sulphate as sodium chloride does. The use of sodium carbonate was discontinued after the twelfth experiment as Barlow[1] has shown that as far as the absorption of sulphur is concerned soda can be omitted when magnesia is present.

---

[1] The determination of sulphuric acid by means of barium chloride in the presence of interfering substances. Report of the Sixth International Congress of Applied Chemistry, 1906, p. 347. Allen and Johnston, THIS JOURNAL, 32, 606, state that the increased loss is due, not entirely to the slightly greater solubility of the barium sulphate in potassium chloride, but to the loss of "free sulphuric acid" from the precipitate on ignition or more exactly, the loss due to the volatilization of the "free sulphuric acid" is greater than that due to the solubility of the barium sulphate in the potassium chloride present. However, in their article in *J. Ind. Eng. Chem.*, 2, 199 they state that in rapid precipitation "the quantity of free sulphuric acid is lowered and under certain conditions practically vanishes."

The values obtained by these different methods rarely approached those by the peroxide method nearer than 0.1 per cent., which suggested that the latter may be too high. It was therefore decided to examine a new lot of samples by the peroxide method, fuse the barium sulphate obtained with soda, reprecipitate, and determine the sulphur by the proposed method. The results obtained are given in Table 1.

It appears that the first precipitation of the sulphuric acid by this method gives values very nearly approaching those obtained by fusing the barium sulphate obtained by the peroxide method and reprecipitating. The differences between the two sets of results thus obtained range from —0.04 + 0.11 per cent. (an average of 0.04 per cent.) as given in the last column of Table 1; these differences are within the experimental error.

THE INVERSION OF CANE SUGAR BY INVERTASE. V. THE DESTRUCTION OF INVERTASE BY ACIDS, ALKALIS, AND HOT WATER.

BY C. S. HUDSON AND H. S. PAINE.

Received June 15, 1910

Measurements of the Rate of Destruction.—In a previous publication[2] it was shown that invertase is destroyed by both acids and alkalis. At the temperature of 30° the destructive action became noticeable first at the acid concentration of 0.01 normal and rapidly increased with the acid strength, becoming almost instantaneous at 0.05 normal; the alkaline destruction began a little below 0.01 normal and became almost instantaneous at 0.045 normal. It is to be supposed that at lower temperatures these rates will all be smaller and that at such temperatures a stronger acidity or alkalinity will be required for a noticeable destructive action. On the other hand, at higher temperatures the rates of destruction will doubtless be greater and the destructive action will be noticeable for weaker concentrations of acidity and alkalinity. At a sufficiently high temperature the acid and alkaline ions of water itself will doubtless cause a noticeable destructive action of pure water on invertase. It has long been known that hot water destroys invertase and other enzymes; as these views appear to correlate this destruction by hot water with the destruction by acids and alkalis at low temperatures, measurements were made for the purpose of tracing the destructive action of these three agents at different temperatures, in order to learn in what manner the actions are related. The measurements were made by the procedure that was described in the former publication; the results being recorded in Table 1 and shown graphically in Fig. 1. The recorded rates of destruction are the velocity coefficients of the unimolecular destruction reaction, multiplied by 1,000, the units of measurement being minutes and decimal logarithms.

---

[1] Losses of sulphur on charring, THIS JOURNAL, 26, 354 (1904).

[2] THIS JOURNAL, 32, 774 (1910).

TABLE 1.—RATES OF DESTRUCTION OF INVERTASE BY ACIDS, ALKALIS, AND WATER AT VARIOUS TEMPERATURES

Temperature.	Concentration of hydrochloric acid.	Rate of destruction.	Concentration of sodium hydrate.	Rate of destruction.
0°	0.03 normal	1	0.03 normal	2
	0.04	3	0.04	5
	0.06	9	0.05	17
	0.08	34	0.06	42
	0.10	99	0.08	125
15°	0.03	3	0.03	9
	0.04	10	0.04	38
	0.05	19	0.05	136
	0.06	55	..	...
30°	0.015	1	0.01	3
	0.02	5	0.02	11
	0.03	42	0.03	50
	0.04	96	0.04	245
	0.05	365	..	...
45°	0.01	1	0.01	12
	0.02	26	0.02	41
	0.03	772(?)	0.025	128
60°	0.005	7	0.001	14
	0.0075	18	0.0025	146
	0.01	152	Distilled water	1
65°	0.002	233	0.0001	91
	0.003	301	0.0002	210
			Distilled water	74

The results may best be interpreted from a consideration of the figure; it is seen that as the temperature is raised the rate of destruction by acids and alkalis increases until finally at or about the temperature of 60° distilled water itself slowly destroys invertase, and at 65° the destruction by water is quite rapid. It is evident that the destruction of invertase by hot water is due to the same cause as is its destruction by acids and alkalis. The latter reactions are doubtless hydrolyses of the complex enzyme molecule and it is therefore to be concluded that *the destruction of invertase by hot water is caused by a hydrolysis of the enzyme.* This conclusion doubtless applies to other enzymes also. As far as is known this is the first evidence offered to explain the cause of the well-known destruction of enzymes by hot water. This point of view explains why dry enzyme preparations can be heated without destruction to temperatures over 100° in case no water is present; the hydrolysis does not then take place.

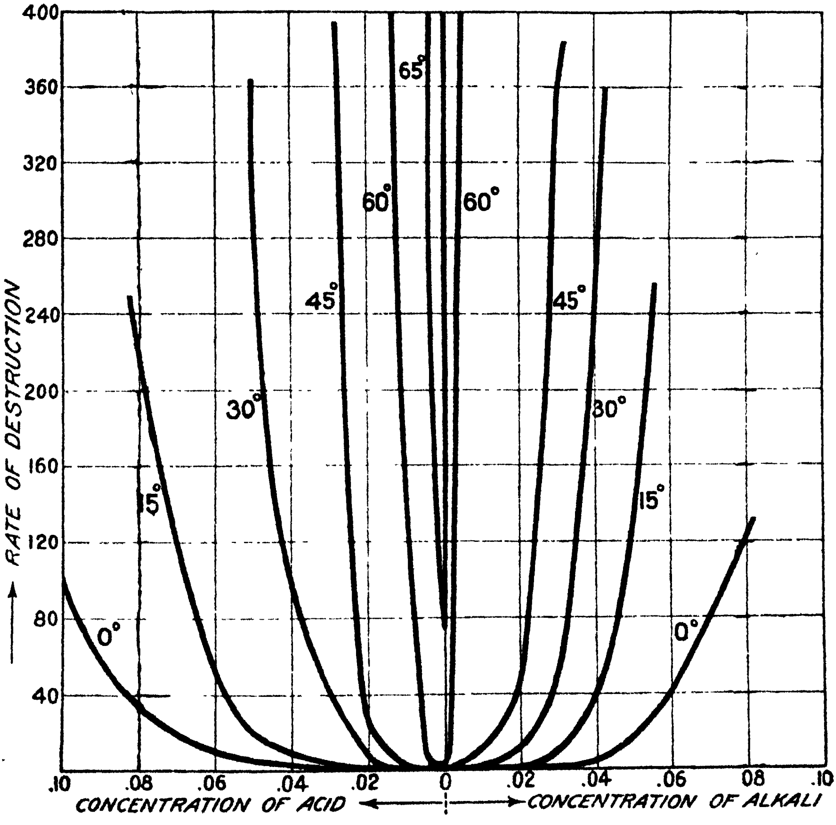


Fig. 1.—The rates of destruction of invertase by acids, alkalis, and water, at various temperatures.

The Influence of Temperature in Increasing the Rates of Destruction.—In Table 2 the rates of destruction in the same medium at different temperatures are compared, and in the last column the coefficient which shows how many fold the rate increases for 10° rise in temperature is recorded. Some of the very large and very small rates do not agree with the general average in showing a coefficient of the value of 2–4, but the limits of error in these cases are larger. The average value of the coefficient is 3.1, which agrees with the general observation that this factor for most chemical reactions varies between 2 and 4. The hydrolytic destruction of invertase by acids, alkalis, and hot water thus falls in with the common types of chemical reactions.

TABLE 2.—THE TEMPERATURE COEFFICIENT OF THE DESTRUCTION.

Temperature interval.	Concentration.	Rates.	Coefficient for 10° rise.
0–30	0.04 HCl	3– 96	3.2
0–15	0.06 HCl	9– 55	3.3
0–30	0.03 NaOH	2– 50	2.9
0–30	0.04 NaOH	5–245	3.7
0–15	0.05 NaOH	17–136	4.0
30–45	0.02 HCl	5– 26	3.0
30–45	0.01 NaOH	3– 12	2.5
30–45	0.02 NaOH	11– 41	2.4
Average			3.1

The Protective Action of Fructose against the Destruction of Invertase.—In a forthcoming article the authors will show the very marked effect of cane sugar in protecting invertase from destruction by alcohol; experiments are now described which show that fructose shares with cane sugar this remarkable property, and also protects invertase from destruction by acids and alkalis. The latter protective action has not yet been tested for cane sugar. The experiments were made by the usual procedure, the rate of destruction being measured first in the absence of fructose and then with it present in the concentrations of 2.7, 5.4, and 10.9 per cent. The data are recorded in Table 3 and the action of fructose in protecting invertase from acid destruction is shown in Fig. 2.

TABLE 3.—THE ACTION OF FRUCTOSE IN PROTECTING INVERTASE FROM DESTRUCTION BY ACIDS, ALKALIS, AND HOT WATER.

Temperature.	Concentration of destroyer.	Concentration of fructose.	Rate of destruction.
30	0.04 *N* HCl	0.0	100
		2.7	26
		5.4	12
		10.9	2
30	0.03 *N* NaOH	0.0	100
		2.7	3
		5.4	3
		10.9	4
30	50 per cent. alcohol	0.0	100
		2.7	1
		5.4	1
		10.9	1
61	Distilled water	0.0	100
		2.7	32
		5.4	16
		10.9	24

The rates of destruction given in the table are expressed as per cent. of the rate for the destroyer when no fructose is present. The rates actually found when no fructose is present, expressed as velocity coefficients of the unimolecular destruction reaction, using minutes and decimal logarithms, are 0.04 normal hydrochloric acid, 0.096; 0.03 normal sodium hydroxide, 0.050; 50 per cent. alcohol, 0.85; and water, 0.0052.

It will be seen from the figure that the protective action of fructose in the case of hydrochloric acid is not at all proportional to the concentration of the sugar but approaches a limiting value asymptotically. The limiting value for the protection seems to have been reached in the case of the alkaline solutions and the alcohol with only 2.7 per cent. fructose; this is probably also true for the protection from hot water because the measurements in this case are very difficult to perform accurately, and the values found--32, 16, and 24—do not differ far beyond the possible error.

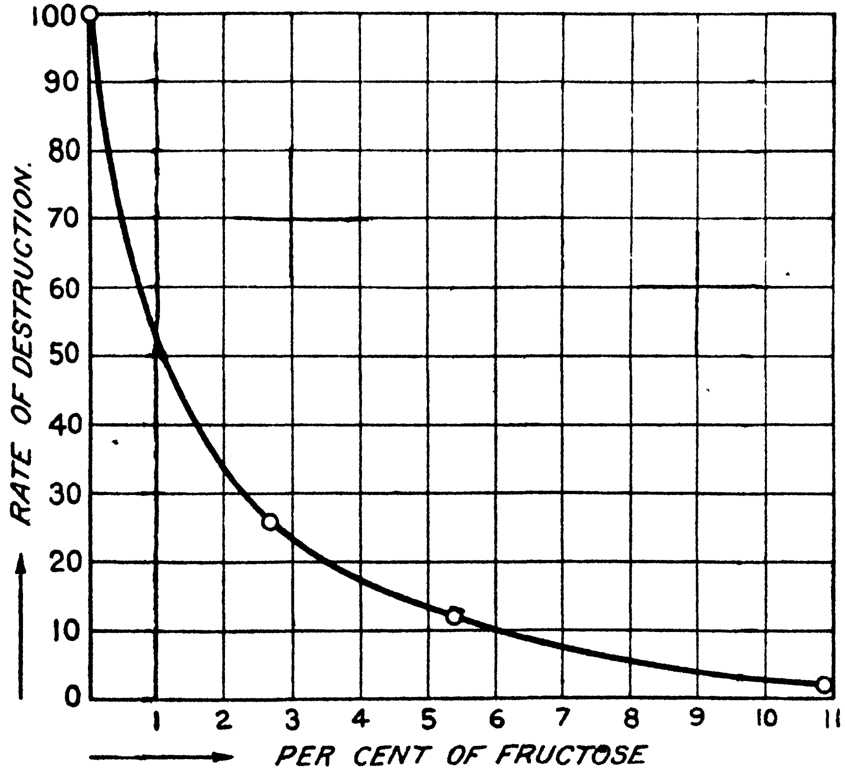


FIG. 2.—The action of fructose in protecting invertase from destruction by acid.

These results on the protection of invertase by fructose can doubtless be interpreted best by assuming that the enzyme forms a combination with the sugar which is more resistant to the destructive action of acids, alkalis, hot water, and alcohol than is invertase itself.

BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE,
WASHINGTON, D. C.

OUTLINE OF A THEORY OF ORGANIC CHEMISTRY FOUNDED ON THE LAW OF ENTROPY.[1]

By Arthur Michael

Received June 27, 1910

There appears to be no generalization in science more firmly established than the second law of thermodynamics, which demands that every spontaneous chemical change shall be accompanied by an increase of entropy, and that the system shall endeavor to realize this increase to its maximum extent.

Since the law of entropy represents the fundamental principle, underlying and regulating all chemical phenomena occurring in nature, it must necessarily be the correct scientific basis for the theory of organic chemistry. But it is a curious fact that there has been as yet little attempt to use this basic chemical principle in connection with organic theory; this theory has been developed along lines so mechanical in their character that it is perhaps no exaggeration to speak of them as essentially pictorial. This unilateral, mechanical development is due largely to the interpretation of the phenomenon called valency; and, if we are to incorporate the law of entropy into chemical theory, it is here that our theoretical conceptions will require a radical modification.

Before entering a discussion of the subject of valency, we shall mention a conception of the chemical genesis of matter, since it prepares the way for the theoretical views which follow. A simple hypothesis is to assume that cosmos was originally made up of two kinds of matter, which were the carriers of two kinds of chemical energy,[2] and that the temperature of the system was inconceivably low. Chemical energy, as it now appears to us, exists in two conditions. One of these is freely and perfectly convertible into less active chemical energy and into various forms of physical energy; and this less active chemical energy can be reconverted into the active form only partially and then with comparative difficulty. We shall designate the active form free, the relatively inactive form, bound *chemical* energy,[3] and, as the transformations of chemical energy must have obeyed the law of entropy since the beginning of cosmos, the original corpuscles were exclusively carriers of free *chemical* energy, and the accumulation of bound *chemical* energy and the various forms of physical energy now existing have been gradually evolved from it.

---

[1] Address delivered at the Second Decennial Celebration of Clark University, Worcester, Mass., September 15, 1909.

[2] To distinguish between them they will be called positive and negative, but this does not imply any connection with positive and negative electricity.

[3] The terms free and bound *chemical* energy, as here used, are not to be confused with the terms free and bound energy as used in physical chemistry, with which they are not identical.

The permanence of the law of entropy justifies the conclusion that the chemical relations which existed between the corpuscles at the beginning were similar to those which now exist between the atoms and the molecules. We may, therefore, assume that the free *chemical* energy of unlike and like corpuscles united to form aggregations in which the corpuscles were held together by bound *chemical* energy. At first the chemical evolution of matter must have been accompanied by an enormous rise of temperature, but later, owing to the decreasing amount of free *chemical* energy in the cosmical system, a period must have come when the loss of heat through radiation was greater than its formation, and then the temperature of the system must have begun to decrease. We may assume, too, that the atoms of those elements, the molecules of which now show the greatest stability toward heat were formed first and during the hottest period of cosmical evolution. Hence, the atoms of hydrogen, and those of the non-metals, with small atomic weight, represent the earliest forms of atomic matter.

If we suppose that in the formation of the atoms of certain elements the free *chemical* energy of the corpuscles was very largely converted into bound *chemical* energy and heat, their atoms would be extremely inert toward other atoms and incapable of uniting with each other. Such elementary matter is represented by the so-called noble gases, in the atoms of which the relation of free corpuscular to free atomic *chemical* energy is analogous to that of free atomic to free molecular *chemical* energy in the atom and molecule of nitrogen. Further, if we suppose that thermic, or other conditions, toward the end of the corpuscular period of chemical evolution no longer permitted a sufficient conversion of free into bound *chemical* energy, we get a glimpse into the genesis of radioactive matter, the atoms of which contain so much free corpuscular *chemical* energy that they represent a reversible system and are, therefore, gradually breaking down into smaller parts, which then rearrange according to the changed conditions of cosmos.

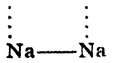
Kekulé,[1] in his memorable paper, "Ueber die Constitution und die Metamorphosen der chemischen Verbindungen," assumed that the first phase in chemical union consists in molecules attracting each other through their chemical affinity, and that a sort of loosely joined, larger molecule is thus formed. It is obvious that the formation of this "Kekulé polymolecule"[2] is due to the attraction between the free *chemical* energy in the constituent molecules, and that it proceeds with the conversion of more or less free into bound *chemical* energy and heat—the extent of this change determining its stability.

Let us represent the free *chemical* energy in an atom by a point and the bound by a line, and let the number of the points and the length of the lines be a rough indication of the changes in the energy values occurring during the reaction. If we assume that the energies of unlike character in a molecule of sodium and of chlorine are approximately equal in value, we may represent the energy relations in sodium and chlorine by

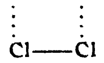
---

[1] *Ann.*, 106, 141

[2] Michael: *Ber.*, 34, 4028; 39, 2140, 2570. Am. Chem. J., 39, 3; 41, 120.

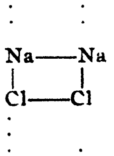


$\mathrm{Na{-\!\!-}Na}$



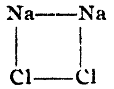
$\mathrm{Cl{-\!\!-}Cl}$

and the "polymolecule," representing the first phase in their interaction, by



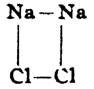
$\begin{array}{c}\mathrm{Na{-\!\!-}Na}\\ |\quad\ \ |\\ \mathrm{Cl{-\!\!-}Cl}\end{array}$

which indicates that some of the free has been converted into bound *chemical* energy. The free *chemical* energies of unlike character would then strive to neutralize each other as completely as possible, a phase of the reaction that may be represented by



$\begin{array}{c}\mathrm{Na{-\!\!-}Na}\\ |\quad\ \ |\\ \mathrm{Cl{-\!\!-}Cl}\end{array}$

and then, certainly facilitated by the enormous "internal maximum heat of reaction,"[1] the bound *chemical* energies between Na and Na and Cl and Cl would be converted into bound *chemical* energy between Na and Cl and Na and Cl; finally, to realize a phase which may be represented by



$\begin{array}{c}\mathrm{Na{-}Na}\\ |\ \ \ |\\ \mathrm{Cl{-}Cl}\end{array}$

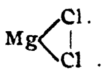
At this point, the bound *chemical* energy between the atoms of like nature may be inadequate to hold them together, and the complex would then break down into two molecules of NaCl.[2]

What happens if we substitute magnesium in the place of sodium; that is, an element the atom of which contains much less positive energy? The formation of a "polymolecule," then the conversion of the free *chemical* energy in the metallic and non-metallic atoms into bound between metal and halogen; but, although the energy in the sodium molecule suffices to neutralize that in the chlorine to an extent that the complex breaks down into two molecules, that in the much less positive magnesium molecule is insufficient to convert enough of the bound energy between the chlorine atoms into bound energy between metal and halogens, therefore the latter atoms separate. On the other hand, the greater energy in the chlorine atoms is capable of using up that in the magnesium to an extent that these fall apart. In magnesium chloride, therefore, the halogen has a considerably greater content of free *chemical* energy than it has in sodium chloride, and bound *chemical* energy exists not only between it and the metal, but between the chlorine atoms. We may represent these relations by:

---

[1] Wohl, *Ber.*, 40, 2290. That part of the free and bound *chemical* energy is converted into heat has not been indicated.

[2] The energies in two unlike atoms are never capable of exactly neutralizing each other, so that a certain content of free *chemical* energy is invariably present in the atoms of every molecule.



While the energy in a molecule of magnesium is not sufficient to separate the chlorine atoms, it obviously may be able to do so with the less negative oxygen, and, if the opposite energies in magnesium and oxygen approximately neutralize each other, two molecules of magnesium oxide should be formed. But, if we take oxygen and a metal with considerably more positive energy than magnesium, say lithium, the oxygen is not able to separate the metallic atoms, while the latter can separate the oxygen atoms, thus leading to the formation of Li_2O, in which the Li atoms are held together by bound *chemical* energy. The valency of an element, according to this interpretation, represents the resultant of the intramolecular chemical forces acting on the atom in terms of *bound chemical* energy, whether the action takes place directly, that is through direct union of the atoms or through space; or indirectly, that is, through other atoms. In as far as the free *chemical* energy in the atoms is not so converted into bound *chemical* energy, it will be able to exert readily a chemical attraction for such other atoms, either in the same or other molecules, for which it shows a chemical affinity.

Although a spontaneous chemical change can proceed only with increase of entropy, the increment depends on free *chemical* energy and chemical affinity existing between those atoms, which in the reaction enter into direct union with each other. The atoms in a molecule are held together *solely* by bound *chemical* energy and, if their chemical nature is such that their free *chemical* energy has very largely disappeared in the formation of the molecule, the substance must be chemically inert; if not, it will be more or less chemically active. Thus, the well neutralized condition of NaCl and Al_2O_3, the superabundant positive energy in Na_2O, and the negative in $AlCl_3$, is reflected in the properties of those substances.

Let us suppose that we could isolate and experiment with elements other than the noble gases in atomic condition, and could prevent the formation of molecules by the union of like, but not of unlike, atoms. In such a system free *chemical* energy would be amply present and chemical union would therefore depend alone on the affinity relations of the atoms. Moreover, if an isomeric substance could be formed, it would be that particular isomer which would represent the maximum entropy of the system under the prevailing conditions.

For instance, the present structure theory indicates the existence of two isomeric cyanogen chlorides, *i. e.*, ClNC and ClCN, but leaves us entirely in doubt why only one is known. So great is the uncertainty in regard to its constitution that this has long been a subject of active discussion and investigation.[1] Chlorine, nitrogen and carbon in atomic condition would possess ample free *chemical* energy for union and the question which isomer would be formed would depend on the increase of entropy connected with the affinity relations of Cl for N and for C. Since we know that the affinity between Cl and N is exceedingly slight, and that between Cl and C is large, it is absolutely certain that the isomer in which the halogen is united directly to the C, *i. e.*, ClCN, would be the direct product. Furthermore, a consideration of the energetic conditions enables us to predict the properties of the isomeric form (ClNC); it could exist only at a very low temperature and under ordinary condition the rearrangement ClNC ⟶ ClCN would occur so quickly, and with such a great increase of heat that the substance would be a violent explosive.[2] The matter we actually deal with is, however, in a molecular condition and all chemical changes that do not proceed *solely* through expenditure of free *chemical* energy involve an expenditure of energy due to overcoming bound *chemical* energy between atoms in the molecule. Chemical action is dependent, therefore, on a third factor, which constitutes a chemical hindrance, and it can proceed spontaneously only when the increase of entropy due to changes of free *chemical* energy and affinity is greater than the expenditure of energy necessary to overcome the chemical hindrance. That is, when the value of the equation: chemical affinity plus free chemical energy divided by chemical hindrance, is positive.

To ascertain quantitative values for the various factors that determine an organic reaction is at present impossible, but it is of the greatest importance for the development of organic theory to be able to connect changes in these values with modifications in structure. This done, we shall then be able to predict relative changes in the factors that contribute to the entropy values and thus be able to understand and explain organic reactions to a degree at present impossible.

---

[1] See Michael and Hibbert, *Ann.*, 364, 69.

[2] It is evident that the content of free *chemical* energy in ClNC would be vastly greater than that in ClCN, which implies a better condition of intramolecular neutralization of the chemical forces of the atoms in the latter structure. Since such chemical neutralization proceeds with increase of entropy, we may substitute chemical neutralization in the place of entropy in the second law of thermodynamics. Further, we may apply the Carnot principle to the activity of free *chemical* energy of unlike kinds, and conclude that the increase of entropy will be greatest when the chemical forces are able to neutralize each other exactly. This law of chemical neutralization has the advantage over that of entropy in a much wider application to organic reactions (Michael, *J. prakt. Chem.*, [2] 60, 293; 68, 489. *Ber.*, 38, 23).

What are the properties of carbon on which the existence of this wonderful and intricate organic world mainly depend? First, its capacity to polymerize, to form stable chains of astonishing length: second, the extreme sensitiveness of its properties to the influence of other elements,[1] which is shared in a like degree only by hydrogen, and which has been called its "chemical plasticity";[2] and third, its high valence combined with its marked affinity for hydrogen and for most of the non-metals, to form more or less stable derivatives.

The first of these properties stands clearly in a close relation to the position of the element in the periodic system. In the halogen group, the tendency to form greater than diatomic molecules is not shown, with the exception perhaps of iodine; in the oxygen group it is shown by that element, but in a far greater degree by the other members. From analogy, a similar tendency to form large molecules by conversion of free into bound *chemical* energy should be expected in passing from oxygen to nitrogen, but the latter element acts anomalously, although in the formation of its diatomic molecule its free is converted into bound *chemical* energy to a remarkable extent

The next member of this group, phosphorus, shows a marked capacity to polymerize to large molecules, and the conversion of ordinary into red phosphorus, which is accompanied by the evolution of only 19 calories, is one of the most salient illustrations in chemistry of how a change of free into bound *chemical* energy will radically change the properties of a substance. The very existence of organic life depends on carbon not sharing with nitrogen the property of polymerizing to a diatomic molecule, which is poor in free *chemical* energy. The actual change in passing from N to C is similar to that in going from N to P, but it is in a degree much more highly developed, and carbon represents among elements the greatest capability to use the free *chemical* energy in its atom to form molecules containing a large number of atoms. The midway position of carbon in the second series of the periodic system indicates that there is an approximate balance of positive and negative corpuscles in the make-up of its atom. And, as the polymerizing capacity of non-metallic atoms increases, generally speaking, with a tendency toward this constitution of their atoms, it seems reasonable to connect this all-important property of the carbon atom with its corpuscular composition.

A relation which is hardly less important for organic theory than the foregoing, is to what extent the polymerizing power of carbon is modified by the presence of other elements in the molecule, and the influence which they exert on the affinity of carbon for hydrogen and for non-metals. Without exception, every element joined to carbon decreases its polymerizing capacity, *i. e.*, its affinity for itself, and the influence is in the order, H, halogen, N, S and O. To the influence of the last element carbon is so exceedingly sensitive that, through direct union with a single atom of oxygen, the enormous combining capacity of the carbon atom for itself is completely destroyed.

---

[1] Van't Hoff, Ansichten über organische Chem., I, 280; II, 242.

[2] Michael, *J. prakt. Chem.* [2], 60, 325.

Notwithstanding the considerable content of free *chemical* energy in the atoms of CO, this substance shows practically no tendency to polymerize, but the characteristic property of carbon reappears at once, when the influence of oxygen is neutralized by the presence of other elements. Thus, the action of potassium on CO leads not to COK, but to a polymerized product, derived from benzene.

Not only does O decrease the affinity of C for C, but of C for H and for any non-metal to which carbon may be joined, whether the atoms are directly or indirectly joined. This is true to a degree directly proportionate to the extent of such negative influences acting on the atoms.[1] The capacity of hydrogen to decrease the affinity of carbon for carbon is far less than that of oxygen, but it plays, nevertheless, an important role in many organic reactions. Thus, the pinacone ⟶ pinacoline rearrangement: $(H_3C)_2=C(OH)-(HO)C=(CH_3)_2 \longrightarrow (CH_3)_3\equiv C-CO-CH_3+H_2O$, takes place on boiling with dilute mineral acid, and the reaction apparently should lead, with loss of water, to the formation of tetramethylethylene oxide.

---

[1] Michael, *J. prakt. Chem.*, 37, 473; 60, 286. *Ber.*, 38, 28, 3221. The writer is unaware of any facts in organic chemistry which are not strictly in accordance with the above stated rule. W. A. Noyes (THIS JOURNAL, 31, 1371) believes that the greater instability of acetoacetic acid ($CH_3COCH_2CO_2H$) over pyrotartaric acid (CH_3COCO_2H) "is some slight indication that the separation of the carbon atoms is ionic in character, taking place more readily when there is a greater contrast between the atoms united together." In the first-named acid, the group C- CO_2H is under the influence of H_2 and a negative, acidic radical (CH_3CO), in the second under a positive radical (CH_3) and O and it is quite in agreement with the above rule that acetoacetic acid splits off CO_2 much more readily than pyrotartaric acid. The writer, also, knows of no satisfactory evidence in favor of the view that any strictly organic reaction is ionic in character (see Michael, *Ber.*, 38, 29; *Am. Chem. J.*, 43, 322; Michael and Hibbert, *Ber.*, 31, 1090); or of any facts that are more easily understood than otherwise by such an assumption. The formation of ethyl chloride from ethyl alcohol and phosphorus pentachloride, while phenol gives partly chlorobenzene, partly phenyl phosphate, is mentioned by Noyes (*loc. cit.*, 1370) as confirming this view. However, when we consider that the chemical hindrance to the formation of a chloride, *i. e.*, the energy necessary to separate hydroxyl from the hydrocarbon radical, is much greater with phenol than with ethyl alcohol, it is obvious that such assumptions as that phenol can ionize to the phenyl and hydroxyl group, and that ethyl alcohol can ionize to ethyl and hydroxyl, do not contribute in any way to make the subject more clear.

This compound contains a three-membered, cyclic chain, which is formed under considerable tension, and, besides, a large number (12) of hydrogen atoms, exerting in a very important position (3) their positive influence on the cyclic carbons. Such a structure cannot represent a very stable substance. On the one hand, there is considerable tension, representing energy in a potential condition; on the other, an extremely insufficient, intramolecular chemical neutralization of the positive by the negative energy in its atoms. The compound may, indeed, be compared to sodium oxide, and shares with that substance a capacity to unite with water, most energetically, and with great increase of entropy. It is apparent that the oxide cannot possibly be formed from pinacone under the conditions of the reaction, but, if a rearrangement may lead to the formation of an intramolecularly well neutralized substance, this may be formed, provided the increase of entropy due to the intramolecular neutralization is greater than the decrease that is due to the chemical hindrance, *i. e.*, the energy necessary to effect the migration of a methyl group. These conditions are possible, for pinacoline represents a fairly well neutralized structure and has, consequently, a considerable heat of formation;[1] and the expenditure of energy accompanying the migration of a methyl in pinacone is comparatively small, owing to the *decrease of the affinity of carbon for carbon` by the influence of the numerous hydrogens.*

That phenyl exerts an extremely strong positive influence on any atom joined directly to it[2] is evident from the fact that two such groups united directly with iodine, give that non-metal a metallic character. It might, therefore, have been expected, that the accumulation of phenyl groups would facilitate rearrangements of the nature of the pinacone ⟶ pinacoline reaction, as this has been especially proven by the investigations of Tiffeneau. We have, moreover, direct experimental evidence that hydrogen diminishes the affinity of carbon for carbon in the observation of Acree,[3] that in the rearrangement with di-*p*-tolyldiphenylpinacone it is the more positive tolyl radical that migrates.

Another interesting illustration of this influence of hydrogen is found in that much-discussed substance "triphenylmethyl" (hexaphenylethane). Tshitshibabin[4] has shown that replacement of five of the hydrogens in ethane by phenyl groups materially lessens the affinity of the ethane carbon atoms for each other. It is, therefore, not surpris-

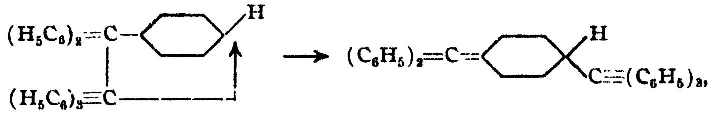
[1] Zoubuff, *Chem. Centralbl.*, 99, I, 516.

[2] Michael and Leighton, *Ber.*, 39, 2792.

[3] *Am. Chem. J.*, 33, 180.

[4] *Ber.*, 40, 367.

ing that when the remaining hydrogen is likewise replaced, the mutual affinity of these carbons is so greatly diminished that the substance easily dissociates into two molecules of triphenylmethyl,[1] and that these carbons, or the carbon, in "triphenylmethyl" joined to the three phenyl groups, have chemical properties similar to those of a very positive metal, for instance, sodium.[2] Nor is it surprising that hexaphenylethane may undergo easily a desmotropic rearrangement into the quinoid form:



or, since the difference in the entropy values of these two forms is slight, that the existence of one or the other form, or a derivative, will depend on the nature of a reagent or even of a solvent.[3]

The remaining fundamental properties of carbon, its high valency and its capability to combine not only with hydrogen but with most of the non-metals to form stable derivatives, are also related to the position of the element in the periodic system. An element acts as monovalent towards H, or Cl, when its energy suffices to neutralize that of H, or Cl, to an extent that the system is incapable of uniting with further atoms of these elements. In passing from F to O, from O to N, and from N to C, the valency for H, or Cl, increases, because the amount of energy in these atoms, able to neutralize that of H, or Cl, is successively decreasing. CH_4 or CCl_4 represent stable substances, because the energy and affinity relations between C and H, or Cl, are such that, in the combination of four atoms of hydrogen or chlorine among themselves and with one atom of carbon, comparatively little free *chemical* energy remains in any of the atoms.[1]

---

[1] Since the above was written Schlenk (*Ann.*, 372, 1) has shown that with a more positive radical than phenyl, *i. e.*, biphenyl, the affinity of carbon for carbon is reduced to such an extent that tribiphenylmethyl exists in solution in mono-molecular condition, which is a further confirmation of the above explanation.

[2] Michael, *J. prakt. Chem.*, [2] 60, 423, 428; 64, 107; *Ber.*, 39, 2791.

[3] Michael and Hibbert, *Ber.*, 41, 1091. A thermochemical investigation on *intramolecular* rearrangement will be published later; it may be stated that all our present experimental data on this subject confirm the view that the fundamental reason of the phenomenon is the increase of entropy proceeding with the change. In *intramolecular* changes it is the formation of an isomer with a greater heat of formation and in *intermolecular* rearrangements the increase of entropy is connected with a change in composition and the reagent uniting with a product of decomposition; in either case, slight chemical or physical forces may bring about the change, if the chemical hindrance is inconsiderable (see Michael and Hibbert, *Ber.*, 41, 1091). The rearrangements of camphor on treatment with P_4O_6 and H_2SO_4, to which W. A. Noyes (THIS JOURNAL, 31, 1372) recently called attention, may be understood from the point of view here presented. In camphor the affinity of the central carbon to those with which it is directly joined has been diminished considerably by the influence of hydrocarbon radicals and the central ring appears to exist in a condition of tension; moreover, such reduced benzene derivatives show a tendency to pass over into benzene derivatives, as the formation of the para-bonds in benzene is connected with a considerable increase of entropy (Michael, *J. prakt. Chem.*, [2] 79, 418). Phosphoric anhydride is a *powerful dehydrating agent* and the formation of a benzene derivative (cymene) with the elimination of water and rupture of a central carbon bond represents the maximum increase of entropy. In its action on camphor sulphuric acid acts not only as a *hydrolyzing*, but also as an *oxidizing agent*; the formation of *p*-acetyl-*o*-xylene undoubtedly represents the maximum entropy under such conditions.

Like the polymerizing capacity and the "chemical plasticity" of carbon, its power to unite not only with hydrogen, but with most non-metals, is due to the approximate balance of the positive and negative corpuscular energies in its atom. The direction in which the affinity of carbon for such elements will vary under the influence of other atoms in the molecule must be toward those of elements adjacent to it in the periodic system. Thus, the effect of increasing the influence of H on C in relation to H, or to a non-metal, joined to it, must be to shift its affinity values toward those of silicon, *i. e.*, there should be a decrease in the value for H and an increase for that of a non-metal. On the other hand, increasing the influence of O should shift them towards those of N, *i. e.*, decrease the values both for H and a non-metal. Further, the effect of such changes on the content of free *chemical* energy of C, and of any atom joined to it, must stand in a direct relation to the changes in the affinity values; in fact, the free must respond to such changes before the bound *chemical* energy.

According to van't Hoff,[2] two atoms in a molecule acting through direct union or through space, or indirectly, that is through intermediate atoms. This idea has been further developed[3] and shown to be of great importance in explaining organic reactions. If we number a certain atom in any fatty compound with a normal carbon chain by the figure 1, our present knowledge of the combined mutual influence between this atom and others in the molecule is expressed by the following "scale of combined influence," the numbers indicating the degree of removal and the extent of the influence decreasing in the order given: 2—3—5—6—4—7—

---

[1] Replacement of an H in CH_4 by Na gives a substance with preponderance of positive energy, and which is, therefore, poorly neutralized intramolecularly. Carbon, a weak non-metal, in uniting with very positive metals, tends to form compounds of the type C_2Me, in which the accumulated negative energy of several carbon atoms endeavors to neutralize the positive energy of the metal. Only with a weak positive metal like Al are metallic derivatives of methane formed, and it is doubtless owing to this relation between the energies of C and Al, the compounds of which are so widely distributed in nature, that we owe the occurrence of such enormous deposits of *saturated* hydrocarbons.

[2] Ansichten üeber die organische Chemie, I, 284–285; II, 252–254.

[3] Michael, *J. prakt. Chem.*, [2] 60, 331. *Ber.*, 39, 2138–2157, 2780–2790; 40, 141.

(9—10—11)—8. It is to be strongly emphasized that the effect of an atom in position 2 or 3 is *far greater* than that of any similar atom less closely connected, and, in the case of atoms farther removed, the influence must be largely direct, *i. e.*, spatial.

The principles developed above form a new basis for the theory of organic chemistry and may be applied to any problem arising in the science.

Several important organic questions will be discussed from the new point of view. One of the weakest sides of the present structure theory is that it indicates the existence of a countless number of compounds, which are incapable of existence. One instance, that of an isomeric chloride of cyanogen (ClNC) has been already discussed, but this question is of such importance that it will be considered with substances of a different type. Nitrosomethane (H_3CNO) does not exist, as it passes over spontaneously into the isomeric oxime: $H_3C—NO \longrightarrow H_2C=N(OH)$. If we add an oxygen to the nitroso group, we obtain nitromethane (H_3CNO_2), which is perfectly stable, but the tautomeric form of which ($H_2C=NO(OH)$) is so unstable, that its existence can be proven only by indirect means. The thermochemical equation, $2NO + O_2 = 2NO_2 + 26.9$ cal. proves conclusively that the nitroso group contains much more free *chemical* energy than the nitro, which is the reason why the nitroso group in nitrosobenzene is so much more reactive than the nitro group in nitrobenzene. In nitrosomethane, then, the following energetic and affinity relations exist: the oxygen has much free *chemical* energy and a strong affinity for the H of the methyl group, and by the change into the oxime, the great content of free *chemical* energy in the nitroso group is largely converted into bound *chemical* energy and heat. The transformation therefore proceeds with increase of entropy and the oxime represents an intramolecularly well neutralized structure, which agrees with its amphoteric properties and the slight additive capacity at the double bond. Since the nitro group in nitromethane has less free *chemical* energy than the nitroso in nitrosomethane, its oxygen has less capability to overcome the bound *chemical* energy holding the hydrogen to the carbon. A rearrangement to isonitromethane is barred for a second reason, *viz.*, that it would proceed with a degradation of entropy, for it is evident that the *neutral* nitromethane, the nitro group of which carries but little free *chemical* energy, is vastly poorer in such energy than the strongly *acidic*, unstaturated isonitromethane.[1]

In order that a rearrangement should proceed spontaneously, the atom which receives the migrating atom, or group, must have sufficient affinity for it to be able to overcome the bound *chemical* energy between the migrating atom, or group, and the atom to which it is already joined.

---

[1] See *Ann.*, 363, 21.

If we increase through a structural change the bound *chemical* energy more than we do the affinity and free *chemical* energy factor; or if we decrease the latter without essentially altering the former, we obviously increase the relative stability of the new derivative and it may show an existence in a free state. Through certain structural changes the difference between the entropy values of the isomeric forms may be lessened, and we may arrive in this way to desmotropic substances, the energy relations of which are so evenly balanced that the existence of one or the other form may be determined by a slight expenditure of extraneous chemical, or physical energy.[1]

Before 1887 the substitution process in organic chemistry was universally supposed to consist of the direct replacement of an atom, or group, by another. It was then shown, by an investigation on the constitution of acetoacetic ester and its sodium derivative,[2] that this view could be upheld no longer and that apparent substitution is often the result of a combination of an addition and elimination process. Subsequent researches[3] have shown that substitution, as represented by the old view is of comparatively rare occurrence, and that a rational interpretation of the process may be based on the entropy principle. Thus, by the use of a metal like sodium, which has considerable free *chemical* energy and a strong affinity for oxygen, the hydrogen in $CH_2=NOH$ attached directly to oxygen may be driven out, with the formation of $CH_2=NONa$.[4] This change is only apparently a direct replacement of hydrogen by sodium, for what actually occurs is, that the energy and affinity values of the metal are such that it is able to overcome the bound *chemical* energy between the oxygen and hydrogen and that the latter element is *driven out*, not replaced.

The distinction between replacing and driving out may seem from the above instance to be unimportant, but it is in reality of fundamental importance in organic reactions. Let us consider, for instance, the behavior of nitromethane and hydrocyanic acid towards sodium from the new point of view! In the system

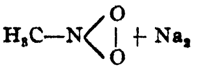
---

[1] Michael, *Ann.*, 363, 27.

[2] Michael, *J. prakt. Chem.* [2], 37, 473.

[3] Michael, *Loc. cit.*, 60, 316. *Ber.*, 33, 3739; 34, 4028; 38, 22, 1922–1938, 2083, 2097, 3218. *Amer. Chem. J.*, 43, 330.

[4] It does not follow from the formation of this sodium derivative that the change as represented by $CH_2=NOH \longrightarrow CH_2=NONa$ designates an increase of entropy; indeed, a consideration of the well neutralized, amphoteric character of the oxime and the strong basic, easily hydrolyzed character of the sodium derivative, leaves no doubt that the free *chemical* energy in the latter is much greater than in the former structure. In the reaction much of the free *chemical* energy in sodium is converted into bound; it is the total change ($2CH_2=NOH + Na_2 = 2CH_2=NONa + H_2$) that proceeds with increase of entropy.



$$H_3C{-}N\begin{matrix}O\\ |\\ O\end{matrix} + Na_2$$

the metal may be attracted either by the C or the O, but not only is the free *chemical* energy in the O larger than that in the C, but also the chemical affinity for Na. Moreover, according to the law of entropy, the system must strive to realize the maximum condition, which will be the formation of a sodium derivative, in which the free *chemical* energy existing in nitromethane and in sodium is converted as completely as possible into bound *chemical* energy and heat. This condition is realized by the direct union of Na with O, since then an almost neutral salt will be formed, while the derivative containing the metal joined directly to C would be strongly basic and have positive energy in great excess. Indeed, if such a derivative as $NaCH_2NO_2$ could be obtained at a low temperature, it would pass over at ordinary temperature spontaneously and with an enormous increase of entropy into $CH_2{=}N(ONa)O$.[1] The intramolecular hindrance, which nitromethane offers to attack, of the Na on the O is the energy necessary to overcome the bound *chemical* energy between a hydrogen and the carbon, which, owing to the strong negative character of the nitro group, is very considerably less than in methane and the reaction therefore proceeds readily.

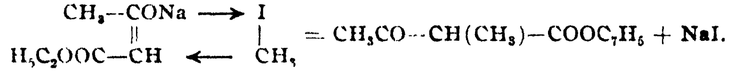
According to the old substitution theory, the action of Na on HCN[2] proceeds by the direct replacement of the hydrogen by the metal, forming NaCN; according to the new theory, the Na may be attracted by the C or the N, and a salt may be formed if the metal is able to overcome the bound *chemical* energy between the H and the C and the reaction proceeds with an increase of entropy. The properties of the cyano group leave no doubt as to the existence of considerable free *chemical* energy in the C and the N, and there is also no doubt that Na has a greater affinity for N than for C: furthermore, N, being an element with more negative *chemical* energy than C, the energy of the metal in NaNC is much better neutralized than it would be in NaCN. The energy and affinity conditions permit, therefore, in the *direct* formation of $CH_2{=}NO(ONa)$ and NaNC, the maximum possible increase of entropy, and any other conception of the structures of these salts, is as inconceivable from the new theory, as the older view leaves us wholly in the dark in regard to them.

---

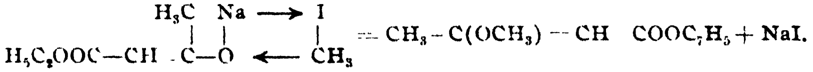
[1] Although a "double" bond is usually an indication of the accumulation of free *chemical* energy, its symbolistic use for this purpose would be misleading. The free *chemical* energy in an atom must vary with the extent of intramolecular neutralization; *i. e.*, in $CH_2{=}NO(ONa)$ the free *chemical* energy at C and N is used up indirectly to a very considerable extent in neutralizing the positive energy of the sodium. An approximate idea of the free *chemical* energy in the atoms of a molecule can usually be formed by a consideration of their chemical nature, the structure and the properties of the substance.

[2] Michael and Hibbert, *Ann.*, 364, 64.

We have seen that the positive energy in sodium has been largely converted into bound *chemical* energy, when the metal is introduced into nitromethane and that neither at the unsaturated carbon or nitrogen of $H_2C=N(ONa)O$ is there much free *chemical* energy. It follows from these energy conditions that this salt should not easily react with a reagent, unless the latter contains atoms with much free *chemical* energy and a large affinity value for certain atoms in the salt. Hence, sodium isonitromethane is comparatively inert toward methyl iodide: but, if we make a change in the structure of the salt, so that the metal is less well neutralized, we shall facilitate the reaction; for, by doing so, we increase not only the free *chemical* energy of the unsaturated atoms, but the difference between the heats of formation of sodium iodide and the sodium salt, which is one of the largest factors in determining the entropy of the reaction. The conditions for an easy reaction are fulfilled, for instance, in sodium acetoacetic ester ($CH_3—CONa=CH—COOC_2H_5$), for in this derivative the positive energy of the metal is very inadequately neutralized by the weakly acidic organic radical to which it is joined, and the unequal balance between the positive and negative chemical forces must leave considerable free *chemical* energy in the unsaturated atoms. The reaction may proceed in two directions:

I. 

$$\begin{array}{lcl} CH_3{-}CONa & \longrightarrow & I \\ \Vert & & | \\ H_5C_2OOC{-}CH & \longleftarrow & CH_3 \end{array} = CH_3CO{-}CH(CH_3){-}COOC_7H_5 + NaI.$$

II. 

$$\begin{array}{lcl} \quad H_3C \quad Na & \longrightarrow & I \\ \quad\;\; | \quad\;\; | & & | \\ H_5C_2OOC{-}CH\;C{-}O & \longleftarrow & CH_3 \end{array} = CH_3{-}C(OCH_3){-}CH \quad COOC_7H_5 + NaI.$$

It is of interest to analyze the energy and affinity relations of the unsaturated carbon joined directly to the carbethoxyl group and those of the oxygen joined to sodium, since they determine the course of the reaction. Sodium iodide is formed in either case, and, as the heat of formation of the C- is greater than that of the O-methyl derivative,[1] its formation represents the maximum entropy of the system. The introduction of sodium into acetoacetic ester ($CH_3—CO—CH_2—COOC_2H_5$) has the following effect on the energy and affinity relations of the carbonyl oxygen (in CO) and the methylene carbon (in CH_2):

First, the free *chemical* energy in the O has been greatly decreased through direct union with the metal, while part of the bound *chemical* energy of the C (used before in holding the eliminated H) has been converted into free; second, the affinity of the O for CH_3 has been greatly reduced by the positive influence of the metal, which, on the other hand, has neutralized the effect of the two negative radicals (CH_3CO and $COOC_2H_5$) and given the unsaturated α-C a large affinity value for methyl. It is evident that when we take the entropy, energy and affinity relations into consideration, the conversion of the O-sodium salt into the C-methyl derivative, *i. e.*, the reaction represented by I, is not an abnormal, but a perfectly normal, reaction,[1] as, indeed is every chemical change in which the condition of maximum entropy is realized.

---

[1] Experimental proof will be published later.

Finally, we shall discuss another fundamental organic process, that of addition, from the standpoint of the second law of thermodynamics.

If we remove one hydrogen from two adjacent hydrocarbon groups in propane a compound is formed ($CH_3—CH=CH_2$) in which part of the bound *chemical* energy previously holding the eliminated hydrogen atoms in chemical union appears as free *chemical* energy at the unsaturated C-atoms.[2] In the addition of a reagent to such a compound, the free *chemical* energy of the unsaturated atoms is more or less completely converted into bound *chemical* energy and heat, and the second law of thermodynamics compels the addition to take place in such a manner that the maximum entropy will be realized, unless there is some chemical hindrance, which prevents this attainment of the ultimate goal of free *chemical* energy.

The structure theory teaches us that in the addition of hydrobromic acid to propene, two isomers (propyl and isopropyl bromide) may be formed; but it fails altogether to give us any indication which of these products, or whether both of them, should result. The chemical hindrance in this reaction is the energy necessary to overcome the bound *chemical* energy between the H and the Br of HBr to the extent to which it exists between them in the bromopropane that will be formed in the addition.[3] This hindrance is obviously quantitatively the same in the formation of either isomer. The maximum entropy in this addition will be attained, therefore, in the formation of the isomeric bromopropane with the greater heat of formation.

Obviously, it is of great importance in this and in many other organic reactions to be able to trace the relation between the structure of isomers and their heat of formation. This is enabled by the following "thermochemical law of structure."[4] In isomers with normal chains and which contain a common negative radical as a nucleus, that isomer will have the largest heat of formation, the positive radicals of which to the greatest extent are under the influence—direct and indirect—of the negative nucleus. Thus, in propyl and isopropyl bromide the common negative nucleus is CBr, which in the last compound is under the direct influence of two methyl groups, while in propyl bromide only one methyl is directly, the other indirectly, joined. The intramolecular neutralization, which finds an expression in the heat of formation, is therefore larger in the iso than in the normal bromide, and, since the thermic value of direct is very much greater than that of indirect chemical union, the heat of formation of the former compound is considerably larger than that of the latter.

---

[1] Michael, *Ber.*, 38, 129.

[2] *J. prakt. Chem.*, [2] 60, 298.

[3] Michael, *Am. Chem. J.*, 43, 333 (footnote).

[4] Michael, *J. prakt. Chem.*, [2] 68, 499; 79, 418; *Ber.*, 39, 2140.

Not only does the system, propene and hydrobromic acid, realize its maximum condition of entropy in the formation of isopropyl bromide, but the affinity relations at the points of maximum concentration of the free *chemical* energy, *i. e.*, at the unsaturated carbons, are such as to favor the course of the reaction in this direction, since the influence of methyl in this substance is positive to that of hydrogen in the same position.[1] This relation causes in propene a greater accumulation of positive energy at the middle than at the end unsaturated carbon and the middle carbon must have, therefore, the greater affinity for the strongly negative halogen of the acid. It seems theoretically probable that this coincidence of affinity and entropy values should lead exclusively to the formation of the iso derivative, as, indeed, it would if chemical change depended solely on the free energy and the affinity values. When a mixture, containing an acid with a very large and a very small acidity constant, is brought together with a quantity of a strong base inadequate for complete neutralization of the acids present, there is always an appreciable amount of salt derived from the weak acid formed. The chemical force in each acid endeavors to its utmost capacity to contribute its share toward the increase of entropy, which depends not only on the values of the affinity constants but, although to a very much smaller degree, on the actual mass, by weight, of acid present.

If the formation of normal propyl bromide from propene and hydrobromic acid proceeds with an increase of entropy, which it undoubtedly does, we have in this addition reaction two chemical forces, each striving to increase the entropy, but, in this case, the mass by weight cannot be changed and the struggle is between energies.[2] Furthermore, since there is no difference in the chemical hindrance. to the addition in either direction, it is extremely probable that the relative amounts of salts, or isomeric bromides, formed will stand in a direct relation to the increase of entropy, and as this is very much greater with the formation of isopropyl bromide, it agrees with the theory that the normal bromide is formed only to a very slight extent.[3]

The principle here involved was first used by Thomson[4] to determine the relative acidity constants, and has been called the "*principle of*

---

[1] Michael, *J. prakt. Chem.*, [2] 60, 332; *Ber.*, 39, 2142 (footnote).

[2] There is no practical difference, as matter from a chemical point of view should be considered only as a carrier of chemical energy.

[3] Michael and Leighton, *J. prakt. Chem.*, 60, 443.

[4] *Pogg. Ann.*, 138, 497.

partition";[1] it may be applied to every organic reaction where two or more isomers may be formed.[2] Let us take, as illustrations of the application of this principle, the addition of water by means of sulphuric acid to hexine–1 and –2. In hexine–1 ($CH_3—CH_2—CH_2—CH_2—C\equiv CH$), we have practically the same conditions as in propene, that is, the difference between the energy and affinity values of the unsaturated carbons are due to the difference between the direct influence of an alkyl group and a hydrogen; hexanone–2 ($CH_3—CH_2—CH_2—CH_2—CO—CH_3$) and probably a very slight amount of hexanal ($CH_3—CH_2—CH_2—CH_2—CH_2—CHO$) are formed. The relations in hexine–2 ($CH_3—CH_2—CH_2—C\equiv C—CH_3$) are quite different; the unsaturated carbons are both joined directly to alkyl groups, and the change in their energy values is due not to direct, but to indirect, influences, which are largely spatial. This relation must cause the heats of formation of the products that may result, hexanone–2 and –3, to be much nearer together than the isomers that may be formed in the addition to hexine–1; also an approximation in the energy and affinity values at the unsaturated carbons.

According to the "principle of partition," the relative amounts of hexanone–2 and –3 formed should not fall very far apart. Moreover, we can approximately estimate the energy values of the unsaturated carbons in relative terms by the use of the "scale of combined influence" mentioned above. Applying this scale to the relations in hexine–2, omitting those atoms the influences of which on the unsaturated carbons are equal,[2] or very nearly so, we find that Δ^β—C[3] (joined directly to methyl) is under the influence of one carbon in the 4th, one hydrogen in the 3rd, and three hydrogens in the 5th position, and Δ^γ—C (joined directly to butyl) has one carbon acting in the 3rd and 4 hydrogens in the 4th position. Since atoms in the 3rd and 5th positions exert a greater influence than those in the 4th, it is obvious that the positive energy at Δ^β—C is greater than that at Δ^γ—C, and that a larger proportion of that ketone should be formed, when the negative part of the addenda adds to it, *i. e.*, hexanone–2. A re-investigation[4] of the reaction shows indeed that about 60 per cent. of hexanone–2 to 40 per cent. of –3 are formed in the reaction.

The present structure theory has been, and always will be, of inestimable service to organic chemistry: it has taught us, until recently,[5] the possible number of isomers that may exist of a given formula, and it has been a guide in determining the constitution of most of the substances that have been discovered. But its weakness and limitations are inherent in its foundation on a mechanical conception of valency and an almost exclusive theoretical development along similar lines, for surely in nature there are no forces more intimately and indissolubly connected with changes in energy than the chemical.

---

[1] Michael, *J. prakt. Chem.*, [2] 60, 341–354; *Ber.*, 39, 2138–2156, 2569, 2786–2795; 40, 140.

[2] See *J. prakt. Chem.*, 60, 341. *Ber.*, 39, 2141.

[3] The capital "Delta" denotes unsaturation (Baeyer, *Ann.*, 245, 112).

[4] Michael, *Ber.*, 39, 2133.

[5] *Ber.*, 39, 203.

Largely for this reason, the structure theory fails to offer explanations for many of the simplest organic reactions and, for many years, it has failed in explaining and co-ordinating with theory much of the wonderful experimental progress that has been made in the science.

It is true that innumerable attempts have been made to amplify or change the idea of valency and the structure theory so as to remedy these deficiencies, but they have always been along mechanical lines and have led to such impossible theoretical conceptions as new brands of valencies, dissociated and partial valencies, oxonium and carbonium theories, steric hindrance due to size of the atoms, etc., etc.

All the forces in nature, whether mechanical or chemical, have the same goal in view, which is the realization of the maximum condition of entropy, and a scientific theory of chemistry must inevitably have this law as its basis. The present aim of organic theory is not to abandon the structure theory, but so to broaden and develop it that it becomes a consistent and harmonious part of nature.

NEWTON CENTRE, MASS

NEW BOOKS.

The Elements of the Science of Nutrition. By GRAHAM LUSK, Ph.D., M.A., F.R.S., (Edin). Second edition. W. B Saunders Company: Philadelphia, 1910. 402 pages, illustrated. Cloth, $3.00 net.

The science of nutrition attracts attention at the present time from the physiologist, the chemist and the practicing physician, but whatever his interest may be, the man who wishes to follow the developments of that science of to-day must have at his command a good knowledge of modern physiological chemistry. This truth is well illustrated in the book in question.

The science of nutrition, like many other sciences, goes back to Lavoisier for its beginning, and in an interesting introductory chapter Lusk traces the cardinal points in its growth down to the present time. The author is a well-known physiologist and has himself made valuable contributions to the field. He has condensed into some four hundred pages a very clear and interesting résumé of the noteworthy literature of the subject. The book is divided into fifteen chapters which discuss the uses and effects of various kinds of foods, the relations to temperature and to work, the products of metabolism and other questions which properly belong in such discussions. The treatment is much fuller and more satisfactory than is usually found in works on physiology which, in a way, cover the same ground. Very good literature references add greatly to the value of the explanations. Three chapters, the 12th, 13th and 14th, are devoted to the discussion of our present views on metabolism in diabetes, metabolism in fever and the purine metabolism in its relations to gout and other conditions. It is pointed out by the author that the rapidly accumulating data bearing on these topics may soon make possible rational theories as to the origin of these diseases. The interesting relation of the purine chemistry to this field of study is pointed out at length.

This book can be heartily recommended to any one who wishes a textbook guide with which to work into an understanding of the present status of the science of nutrition. J. H. LONG.

RECENT PUBLICATIONS.

ARHENNIUS, S.: **Lehrbuch der Electrochemie.** Deutsche Ausgabe von H. Euler. Neuer Abdruck. Leipzig: 8°, 313 pp., 8 M.

ARTHUS, M.: **Précis de Chemie Physiologique.** 6. édition, augmentée. Paris: 8°, 403 pp., 5 M.

BATTELLI, A., OCCHIALINI, A., u CHELLA, S.: **Die Radioaktivität.** Aus dem Italienischen übersetzt von M. Iklé. Leipzig: 8°, 428 pp., 6.40 M.

BAUCKNER, J.: **Chemische Grundgesetze u. Grundbegriffe, berarbeitet durch Schülerübungen.** Diessen: 8°, 104 pp., 2 M.

BERTHELOT UND PÉAN DE SAINT-GILLES: **Untersuchungen über die Affinitäten. Ueber Bildung und Zersetzung der Aether.** Leipzig: W. Engelmann. 8°, 242 S., 4.40 M.

BINZ, ARTHUR: **Ursprung und Entwicklung der chemischen Industrie.** Berlin. G. Reimer, 80 Pf.

BLANCHARD, A. A.: **Synthetic Inorganic Chemistry**; a laboratory course for first year college students. 2nd ed. New York: J. Wiley & Sons. 151 pp., $1.00.

BOURQUELOT, E.: **Le Centenaire du Journal de Pharmacie et de Chemie.** Paris: Doin et Fils. Octave.

CARTER, H. A.: **Ramie China Grass.** The new textile fibre and all about it. Technical Publishing Co. 8°, 154 pp., 5 s.

CODOUNSKY, FRANZ.: **Bierbrauerei.** Hannover. Jänecke, 4.60 M.

CORDEIRO, F. J. B.: **The Atmosphere, its Characteristics and Dynamics.** 4. 10 s., 6 d.

DAVIDGE, H. T.: **Optical Instruments Simply Explained.** London: Marshall & Co.

DENNSTEDT, M.: **Die Chemie in der Rechtspflege.** Leipzig: 8°, 432 pp., 18 M.

DESCH, CECIL H.: **Metallography.** London: Longmans, Green & Co.

DUBOUX, M: **Contribution a l'analyse physico-chimique des Vins.** Lausanne: 8°, 70 pp.

EMMERICH, G. H.: **Lexikon für Photographie u. Reprodukiionstechnik.** I. Hälfte. Wein: gr. 8, ss., 1-480, 5 M.

FERCHLAND, P.: **Die elektrochemischen Patentschriffen der Vereinigten Staaten.** Bd. [illegible] Elektrothermische Verfahren und Apparate; Entladungen durch Gase. Wilh. Knapp: Halle a/S, 12 M.

FERRARI, D.: **Il trattamento naturale ed artificiale delle acque da fogna, secondo i modermi sistemi di epurazione biologica.** 2 Vol. Parma: L. Battei, 4, 25 L.

FOSTER, C. LE NEVE.: **Treatise on Ore and Stone Mining.** 7 edition. London: 8°, 832 pp., cloth, 29 M.

FRESENIUS, H.: **Chemische Untersuchung der Georgen-, Marien-, Wiesen-, Mariannen- und Friedichs-Quelle zu Bad Landeck.** Wiesbaden: C. W. Kreidels.

GILG, E.: **Lehrbuch der Pharmakognosie.** 2, vermehrte Auflage. Berlin: gr. 8, 384 ss., 8 M.

GMELLEN UND KRAUT: **Handbuch der anorganischen Chemie.** Hrsg. von C. Friedheim und F. Peters. 7 Aufl. Bd. V. 1 Abt. Heidelberg: C. Winters.

HAMMARSTEN, O.: **Lehrbuch der physiologischen Chemie.** 7 Aufl. Wiesbaden: J. F. Bergmann, 23 M

Handbuch der Kaliwerke, Salinen, Tiefbohrunternehmungen und Petroleum-Industrie 1910. Berlin: Kuzen-Zeitung, 12 M.

HARTWIG, C.: **Die menschlichen Genussmittel, ihre Herkunft, Verbreitung, Geschichte, Bestandteile, Anwendung und Wirkung.** (In etwa 16 Lieferungen). Leipzig: gr. 8-Liefg. I, ss., 1-64, Jede Liefg., 2 M.

HÜBENER, E.: **Fleischvergiftungen und Paratyphusinfektionen, ihre Entstehung und Verhütung.** Jena: 8°, 204 pp., 8 M.

Jahresbericht über die Leistungen der Chemischen Technologie, mit besonderer Berücksichtigung der Elektrochemie und Gewerbestatistik für das Jahr 1910, bearbetiet von F. Fischer. Jahrgang 55. Abteilung I: Unorganischer Teil. Leipzig: gr. 8, 669 ss., 15 M.

JÄNECKE, DR. ERNST: **Kurze Uebersicht über sämtliche Legierungen.** Hannover: Max Jänecke, 3.00 M.

JOLY, A.: **Manipulations chimiques.** Analyse qualitative. Notations d'analyse quantitative par liqueurs titrées. Paris: 12, 252 pp., 2 M.

LEYSER, E.: **Die Malz-und Bierbereitung.** II Auflage (3 Bände) Bd. I. Stuttgart: 8°, 535 pp., 12.60 M.

LORENZ, H.: **Lehrbuch der Technischen Physik.** (4 Bände) Bd. III. Technische Hydromechanik. München: R. Oldenbourg, 8°, XXII u., 500 pp., 14 M.

MARR, O.: **Das Trocknen u. die Trockner.** München: R. Oldenbourg, 8°, 10 M.

MCINTOSH, J. G.: **Indiarubber and Gutta-Percha.** Complete practical treatise. By various authors Translated from the French by J. G. McIntosh. 2nd enlarged edition. London: 8°, 424 pp., cloth, 12.80 M.

MELLMANN, P.: **Chemie des täglichen und wirtschaftlichen Lebens.** 2, neubearbeitete Auflage. Leipzig: 8°, 241 ss, 2.75 M.

Methoden der Organischen Chemie. Handbuch für die Arbeiten im Laboratorium. Herausgegeben von T. Weyl. (2 Bände). Lieferung 10 (Bd. II, Liefg. 7). Leipzig: gr. 8, ss. 705-812, 2.80 M.

MEYER, H., UND GOTTLIEB, R.: **Die experimentelle Pharmakologie als Grundlage der Arzneibehandlung.** Wein: 8°, 61 figuren, 12 M.

MEYER, J.: **Die Allotropie der chemischen Elemente.** Sammlung chemischer und chemisch-technischer Vorträge. Stuttgart: W. Herz. Band 15. Heft 2 u. 3. 8°, s., 43-108, 2.40 M.

MUCCIOLI, A.: **Tossicologia forense.** Parte generale. Rome: Loescher & Co., 16, 170 s., 2 L.

OECHSNER DE CONINCK, W. F.: **Cours de Chimie Minérale.** 2 édition. Fascicule 3. Paris: 8°, pg. 345-510, 2 M., L'ouvrage complet, 510 pp., 6.50 M.

OETTINGEN, A.: **Die Schule der Physik, besonders für das Selbstudium verfasst.** Braunschweig: 8°, Leinenband, 11.50 M.

OSTWALD, W.: **Die Schule der Chemie.** Einführung in die Chemie für jedermann. 2, umgearbeitete Auflage. Braunschweig: 8°, 6.40 M.

PECHMANN, H.: **Anleitung zur quantitativen chemischen Gewichtsanalyse nach** C. Zimmermann. 12 Auflage. München: 8°, 67 pp., 2 M.

PELET-JOLIVET, L.: **Die Theorie des Färbeprozesses.** Dresden: 8°, 428 s., 7 M.

PERKIN, F. M.: **Choix de preparations de Chimie Inorganique.** Traduction par E. Mettler. Genève: 8°, 193 pp., 4.50 M.

PORCHER, C., ET NICOLAS, E.: **Cours de Chimie organique et biologique.** 2nd édition. Lyon: 8°, 488 pp.

RIGHI, A.: **La Materia radiante ed i Raggi magnentici.** 2 edizione, aumentata. Bologna: 8°, 7 M.

ROTTGER, H.: **Nahrungsmittel-Chemie.** 4 vermehrte Auflage (2 Bände). Band I. Leipzig: 8°, 611 pp, 11 M.

RUDOLF, W.: **Die Tonwarenerzeugung** (allgemeine Keramik), **mit besonderer Berücksichtigung der chemischen Grundlagen.** Hannover: 8°, 192 pp., Leinenband, 3.60 M.

SAVOIA, H.: **Metallography Applied to Siderurgic Products.** London: 12, cloth, 4.80 M.

SCHÄFER, A.: **Einrichtung und Betrieb eines Gaswerkes.** 3 Auflage. München: R. Oldenbourg, 8°, 18 M.

SCHALL, M.: **Herstellung und Verwendung der verdichteten und verflussigten Gase.** Hannover: 8°, 171 pp., Leinenband, 3.60 M.

SCHIFFERERS: **Praktische Mälzerei- und Brauerei-Betriebskontrolle.** München: R. Oldenbourg, 8°, 15 M.

SCHMIDT, J.: **Jahrbuch der Organischen Chemie.** Jahrgang III. Forschunsergebnisse und Fortschritte im Jahre 1909. Stuttgart: 8°, XX u, 469 pp., 14 M.

SCHÜTZ, E.: **Hüttenmännische Probierkunde.** Wilh. Knapp, Halle a/S: 2 M.

SIMMERSBACH, F.: **Die geologischen Unterlagen des Radiums.** Kattowitz: 8°, 0.80 M.

TIGERSTEDT, R.: **Lehrbuch der Physiologie des Menschen.** 5, umgearbeitete Auflage. Band II. Leipzig: 8°, 519 pp., 12 M. Das jetzt vollständige Werk, 2 Bände, 24 M.

TSCHIRCH, A.: **Handbuch der Pharmakognosie.** (etwa 30 Lieferungen). Leipzig: gr. 8, Lieferung 15-18 pp., 801-1072 (von Band I) Jede Lieferung 2 M. Band I, jetz vollständig, 1082 pp., 36 M.

WALDECK, 2: **Theorie und Praxis des Generatorbetriebes.** Wilh. Knapp, Halle a/S: 3.60 M.

WHITE, ARTHUR S.: **Logic of Nature.** Privately printed.

WITT, O. N., UND LEHMANN, L.: **Chemische Technologie der Gespinstfasern ihre Geschichte, Gewinnung, Verarbeitung und Veredlung.** Band I, Teil 2. Braunschweig: 8°, s., I-XXI und 771-956, 11.50 M. Band I, jetzt vollständig, 977 s., 40 M.

WÜST, F.: **Mitteilungen aus dem eisenhüttenmännischen Institut der Kgl. Techn. Hochschule Aachen.** Wilh. Knapp, Halle a/S: 10 M.

Vol. XXXII. September, 1910. No. 9.

THE JOURNAL

OF THE

American Chemical Society

[Contributions from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 56.]

THE PROPERTIES OF SALT SOLUTIONS IN RELATION TO THE IONIC THEORY.

I. MOL-NUMBERS DERIVED FROM THE FREEZING-POINT LOWERING.

By A. A. Noyes and K. G. Falk

Received June 27, 1910

Contents.

Introduction. 1. Theoretical Considerations. 2. The Experimental Data. 3. Summary of the Mol Numbers Derived from the Freezing-point Lowerings. 4. The Mol Number in Relation to the Type of Salt. 5. Change of the Mol Number with the Concentration.

Introduction.

For a number of years one of the main lines of research pursued in this laboratory, with the aid of grants from the Carnegie Institution of Washington, has been the study of the properties of salt solutions with reference to the well-known anomalies of the ionic theory and with the view of establishing empirically the principles that must be substituted for the inexact theoretical laws ordinarily employed, and, if possible, of finding a rational explanation of the divergences. Such work has also been in progress in many other laboratories, partly with this general purpose, but oftener with more specific ends in view; and there has in consequence been accumulated a large mass of experimental material which has remained to a great extent uncorrelated. It seems therefore highly desirable to subject the existing data to a critical study from the standpoint just referred to; and the present paper is the first of a series of articles which are to be devoted to different phases of this subject.

The factors which according to the ionic theory directly determine the physical properties and also the chemical behavior of salts in solution are: (1) their degrees of ionization, or, in more general terms, the concentrations of the various ions and un-ionized substances present in the solution; (2) the mobilities or conductances of the separate ions; (3) the osmotic pressures of the ions and the un-ionized substances; (4) the so-called active masses or the (by Lewis more specifically defined) activities of the ions and the un-ionized substances; and (5) specific properties characteristic of the separate ions such as their molal volumes, refractive power, etc. Of these factors the first is involved in the interpretation of nearly all properties except those of a distinctly additive nature; the second in that of all phenomena connected with the passage of electricity, such as conductance and transference; the third in that of the so-called molecular or colligative properties, such as vapor pressure, freezing point, and boiling point, and in various thermodynamic relations; the fourth, in the determination of all chemical equilibria and many thermodynamic formulas; and the fifth, in the treatment of the additive and constitutive physical properties and of specific chemical effects, such for example as the catalytic power of the hydrogen ion.

The determination of the values of these separate factors is attended with the difficulty that at least two of them are simultaneously involved in any property of the salt solution that may be measured. From this it follows that a given factor can be determined only with the aid of some assumption in regard to the other factors, or indirectly through the combination of measurements of different properties or of the same property under different conditions. Thus the conductance of a salt depends both on its ionization and the mobility of its ions; and when the ionization is derived from the ratio of the equivalent conductance at the given concentration to that at zero concentration, it is assumed that the mobilities of its ions are the same in the two solutions. Evidence as to the correctness of this assumption may be obtained by the study of some other property dependent upon mobility, such as transference; or by a comparison of the ionization values calculated with its aid with those derived from some independent property, such as the freezing-point lowering.

The first paper of this series will be devoted to the consideration of the freezing-point lowering caused by salts, acids and bases, this being the property from which the total number of mols present in the solution can be most satisfactorily derived.

1. Theoretical Considerations.

In order to calculate exactly the number of mols i resulting from one formula weight of the solute, it is necessary to formulate accurately the theoretical relation between the freezing-point lowering and the molal concentration of the solute. The fact has been recently emphasized by several writers[1] that the most general and exact form of the law of solutions, judging especially from its applicability to non-associating liquids throughout the whole range of concentration, is that expressed by the Raoult vapor-pressure equation:

$$\frac{p}{p_0} = \frac{n_0}{n_0 + n} \text{ or } \frac{p_0 - p}{p_0} = \frac{n}{n + n_0} \qquad (1)$$

where p_0 and p are the vapor-pressures of the solvent ands olution respectively, and n_0 and n are the number of mols of solvent and solute respectively. The thermodynamically corresponding expression for the osmotic pressure P of the solution (neglecting the ordinarily insignificant compression term) is:

$$\log_e \left(1 - \frac{n}{n + n_0}\right) = \frac{PV_0}{RT} \qquad (2)$$

where V_0 is the volume of one mol of liquid solvent, R the gas constant, and T the absolute temperature. A solution which conforms to these laws has been called a *perfect solution.*

It has also been shown by Washburn[2] that the substantially exact numerical expression for the freezing-point lowering Δt which is thermodynamically equivalent to these relations when water is the solvent and the solution is not extremely concentrated is as follows:

$$\frac{n}{n + n_0} = 0.00969\Delta t(1 - 0.0043\Delta t). \qquad (3)$$

For the purposes of this article this may be given the following simpler form, which is obtained by placing $n_0 = 1000/18.01 = 55.5$, solving for n, and writing iN for it:

$$iN = \frac{\Delta t}{1.858}(1 + 0.0055\Delta t), \qquad (4)$$

where N represents the number of formula weights of solute associated with 1000 grams of water, and where 1.858 is the molal lowering in a dilute perfect solution. This expression is in concentrated solutions slightly less exact, but is accurate within 0.1 per cent. for solutions for which $N < 1$ or $\Delta t < 3°$, provided the imperfectly known effect of hydration is neglected.

This expression has been employed in calculating the values of i presented in this article; but in those cases where $\Delta t < 0.20$, and where therefore the parenthesis in the second member differs from unity only by about 0.1 per cent., the parenthesis has been ignored, and the simple formula $iN = \Delta t/1.858$ employed.

---

[1] Compare especially van Laar (Zwei Vorträge über nicht verdünnte Lösungen und über den osmotischen Druck (Vieweg & Sohn, 1906); Lewis, THIS JOURNAL, **30,** 673 (1908); Washburn, *Tech. Quart.*, **21,** 368 (1908).

[2] *Tech. Quart.*, **21,** 373 (1908); and *Jahrb. Radioakt. Elektronik.*, **5,** 493.

The value of i so calculated has a definite empirical significance which is independent of any assumption whatever. It represents, namely, the factor by which the number of formula weights N associated with 1000 grams of water must be multiplied, if the osmotic pressure, vapor pressure, or freezing point is to be correctly calculated by the laws of the perfect solution. The factor i therefore accounts not only for any difference between the number of mols actually existing in the solution and the number of formula weights taken, but also for any physical deviation from the laws of the perfect solution.

Assuming now that there is no such physical deviation—that is to say, that the ions and un-ionized substances are perfect solutes, exerting normal effects in accordance with the laws of the perfect solution, and that the quantity of solvent present is not appreciably diminished by combination with the solute, then evidently the value of i is equal to the number of mols in the solution resulting from one formula weight. Interpreted in this sense i will be called the *mol number* of the solute.

Since there is strong evidence that many salts in solution are hydrated, the assumption that the quantity of free solvent present is the same as that of the pure solvent used in making up the solution is almost always inaccurate. It is therefore important to consider what the magnitude of the error caused by neglecting the effect of hydration upon the value of the calculated mol number is likely to be at different concentrations. Its effect may be readily derived by reference to equation (4) through the following consideration. If, with the N formula weights of solute that are dissolved in 1000 grams or 55.5 mols of water, xN mols of water are in reality combined, the number of formula weights associated with 1000 grams of uncombined water is really greater than the assumed value N in the proportion $55.5/(55.5 - xN)$ or of $1/(1 - xN/55.5)$. The true value of i is therefore smaller than the calculated value in the same proportion; namely, by the following percentage amounts:

Percentage error =	$0.18x$	$0.36x$	$0.90x$	$1.8x$
For N =	0.1	0.2	0.5	1.0

Since x, the mols of water combined with one formula weight of salt, is probably often as large as 5 or 10, there is likely to be in many cases an error in i as large as 1 or 2 per cent. even at a concentration of 0.1 formal; and at much higher concentrations than this, the possible error arising from hydration becomes so large that the interpretation of the values of i as mol numbers has little significance, except perhaps in the case of substances which there is reason to believe are but little hydrated. Provided any independent determination of the true values of i can be found, the results would, however, be of great value in determining the degree of hydration.

The relation of the mol number to the degree of ionization may also be briefly considered. If the only substances present in the solution of a di-ionic[1] salt of the formula BA are the un-ionized substance BA and the ions B^+ or B^{++} and A^- or $A^{=}$, then evidently between the mol-number i and the degree of ionization γ there exists the simple relation

$$i = (1 - \gamma) + 2\gamma = 1 + \gamma. \tag{5}$$

And similarly, if the only substances present in the solution of a tri-ionic salt of the formula B_2A or BA_2 are the un-ionized substance B_2A or BA_2 and the ions B^+ or B^{++} and $A^{=}$ or A^-, then the following relation holds true:

$$i = (1 - \gamma) + 3\gamma = 1 + 2\gamma. \tag{6}$$

And in general for an n-ionic salt, we have

$$i = 1 + (n - 1)\gamma. \tag{7}$$

It is, however, to be noted that the assumption that the un-ionized salt and its simplest ions are the only substances present in the solution is by no means necessarily true in all cases. Thus in the case of tri-ionic salts, like K_2SO_4 or $Ba(NO_3)_2$, it may well be that the intermediate ion, KSO_4^- or NO_3Ba^+ is also present. And in the case of any salt, even of one of the di-ionic type, complex cations and anions and the corresponding complex salt may also be present; thus in a solution of magnesium sulphate there may be present not only $MgSO_4$, Mg^{++}, and $SO_4^{=}$, but also $Mg(SO_4)_2$ and the complex salt $Mg_2(SO_4)_2$; and in a lithium chloride solution not only LiCl, Li^+, and Cl^- but also $LiCl_2^-$ or Li_2Cl^+ and Li_2Cl_2 might be present.

The formation of new substances by reaction with the water is also to be considered; thus in the case of salts of a very weak acid or base (like KCN or ammonium acetate) the hydrolysis-products BOH and HA may be present in considerable quantity, especially in dilute solutions.

2. The Experimental Data.

It is the purpose of this section to bring together the values that have been obtained by various investigators for the freezing-point lowerings caused by salts, acids, and bases; and to derive through a critical consideration of these data what seem to be the best values to adopt. Owing to the many errors in freezing-point measurements, some of which have only gradually come to be recognized, it is in many cases only in this way that fairly reliable results can be secured. Such series of measurements as are obviously affected by unusually large errors have been disregarded.

The method of procedure employed has been to plot the values obtained by each observer for $\Delta t/N$ as ordinates against those of log N as abscissas, where Δt is the observed freezing-point lowering and N is the number of formula weights of salt associated with 1000 grams of water. In cases where the salt content was not so expressed it has been calculated over to this basis. The ratio $\Delta t/N$ will hereafter be designated the *formal freezing-point lowering.* The most representative curve was then drawn through the points representing the data of each observer; and the values of $\Delta t/N$ were taken from the curve at a number of definite concentrations. A mean of the values so obtained from the data of all the observers at each concentration was next derived, assigning to each observer's results a weight based upon the precautions observed in the experimental work, the number of determinations, and the accuracy of the results as indicated by their deviations from the curve. In general, the same weight is assigned to all the results of a given observer; but in a few cases this has been varied for the different substances. This method of assigning weight involves individual judgment and is to a certain extent arbitrary; but it is preferable to assigning equal weight to all the results. The average values so obtained were then plotted in the same way as before, the curve best representing them was drawn, and from this curve the final values of $\Delta t/N$ at definite concentrations were read off.

---

[1] The number of ions into which a salt dissociates will be indicated by the words *di-ionic*, *tri-ionic*, *etc.*; and the valence of the two ions to which the salt gives rise will be indicated by the words *uni-univalent*, *unibivalent*, *bibivalent*, *etc.* Thus $MgSO_4$ is a bibivalent, di-ionic salt; and $K_3Fe(CN)_6$ or $AlCl_3$ is a unitrivalent, tetraionic salt.

The limits of content which are considered are from 0.005 to 0.5 equivalents per liter. For those substances for which the value of $\Delta t/N$ passes through a minimum, the curves were not extended beyond this minimum.

A full discussion of the methods used by the various investigators in determining the freezing points of the solutions will not be entered into. Some of the factors influencing the accuracy of the results will, however, be considered, especially with reference to the relative weights assigned to the data of the different observers.

Passing over the older work as not suitable for the purpose, the investigation of H. C. Jones[1] may be mentioned as the first in which special precautions were taken. He employed a mercury thermometer with a very large bulb which was graduated in thousandths of a degree and could be read to one ten-thousandth, used a large volume (one liter) of solution, stirred moderately, caused a considerable proportion of ice to separate (namely, 1.5 per cent. or that corresponding to an overcooling of 1.2°), and corrected the concentration for the change produced in it by the ice separation. He states that his thermometer readings were reproducible with an average deviation of 0.0002°, but makes no statement as to the standardization of the scale of his thermometer. The concentration was determined synthetically, apparently with sufficient accuracy. His freezing-point vessel was surrounded above and below by felt and on the sides by an air space enclosed by a zinc vessel containing ice and salt. Error doubtless arose from this difference in temperature of the surroundings, but it was probably somewhat reduced by the large volume of solution employed and the fair proportion of ice separated. The results obtained by him with several organic substances in dilute solution are much higher (14–20 per cent. higher at 0.01 normal) than the theoretical values, and indicate the presence of an error doubtless due to failure to secure the true freezing-point. This error may well have influenced his results with the salts to a considerable, though evidently to a much less extent. The weight assigned to the results is therefore unity, this being the value here assigned to data of ordinary reliability.

---

[1] *Z. physik. Chem.*, 11, 110, 523; 12, 623 (1893).

In 1894 Nernst and Abegg[1] discussed the precautions which it was essential to observe in order to obtain the true freezing point of a solution; and a few series of results were published by them and later by Abegg alone.[2] Unfortunately, while the determination of the freezing-point lowerings was unusually accurate, that of the concentration of the solution involved an error, which according to Abegg's statement amounted to 2 per cent. in some cases. The weight assigned to the results is therefore 1.

The work of Loomis,[3] begun about the same time, extended over a number of years and included a large number of compounds. In the author's papers no correction was made for the change in concentration produced by ice separating from the solution. That is shown experimentally to amount to 0.3 per cent in the first paper; and the results for the substances there given (for sodium chloride, magnesium sulphate, and sulphuric acid) have therefore been corrected accordingly. In the work described in the other papers a larger quantity of solution was used; and the probable correction, which was small in any event, was not determined. This cause would tend to make the observed lowerings slightly too large. On the other hand, the method of working, which involved strong stirring and slight undercooling, would result in too small freezing-point lowerings. The inaccuracy in the final results would depend upon these two sources of error, the latter probably being the greater. A weight of 2 or 1 has been assigned to them according to the character of the curve. His results for sodium and potassium hydroxides are so irregular that they have not been included at all.

Barnes determined the freezing-point lowerings caused by sodium and potassium chlorides[4] and hydrochloric and sulphuric acids;[5] and Archibald,[1] using a similar method, determined those of sodium and potassium sulphates. The accuracy was apparently as great as that of the best results of Loomis, and a weight of 2 has therefore been assigned to their results. The results of Hebb[2] with very dilute solutions of potassium chloride were also obtained by a similar method; but a correction was introduced for the ice separating, and the thermometer readings appear to have been more accurate. A weight of 3 has therefore been assigned to them.

---

[1] *Z. physik. Chem.*, 15, 681 (1894).

[2] *Ibid.*, 20, 207 (1896).

[3] *Wied. Ann.*, 51, 500 (1894); 57, 495 (1896), 60, 523 (1898).

[4] *Trans. Nova Scotian Instit. of Science*, 10, 153.

[5] *Trans. Roy. Soc. Canada*, II, 6, [3] 37 (1900).

Ponsot[3] obtained results for a number of compounds, by determining the temperature and concentration of a solution in equilibrium with a large proportion of ice. For potassium bromide no representative curve could be drawn and the results were not employed. For potassium chloride any curve is unsatisfactory, and for potassium sulphate too few results are given within the required range of concentration so that a weight of only one-half was assigned. For the other substances, however, (sodium chloride, sulphuric acid, barium chloride, and lead nitrate), very fair curves are obtained, and a weight of 1 was given to the results.

Raoult[4] obtained two series of results with sodium and potassium chlorides. To his results a weight of 1 in one series and of ½ in the other was assigned as the results are so few in number and so scattered as to make it difficult to draw a satisfactory curve.

The greatest accuracy in determining differences in the freezing points of water and solutions attained up to the time of their publications appears to have been secured by Hausrath[5] and Osaka,[6] who, by measuring the electromotive force at thermoelectric junctions were able to measure differences of a few hundred-thousandths of a degree. That there were difficulties in these measurements is, however, seen from the irregularity of some of the results obtained at very great dilutions. Error in the preparation and standardization of the solutions probably is part of the source of these irregularities. The results down to 0.005 normal used here are fairly regular, except for a few substances; but since the results were not obtained for concentrations greater than 0.035 normal, a satisfactory curve could not be drawn and the experimental inaccuracies are still too large to warrant assigning a higher weight than 1 or in some cases 2 to the results. Their freezing-point lowerings have all been increased in the ratio 1.858/1.85, since 1.85 was used by them as the molal lowering in the standardization.

[1] *Trans. Nova Scotian Instit. of Science*, 10, 44.

[2] *Ibid.*, 10, 409.

[3] *Ann. chim. phys.*, [7] 10, 79 (1897).

[4] *Z. physik. Chem.*, 27, 617 (1898).

[5] *Ann. phys.*, [4] 9, 522 (1902).

[6] *Z. physik. Chem.*, 41, 560 (1902).

A few of the results obtained by Biltz[1] are used. He took all ordinary precautions in his measurements, but worked to a great extent with concentrations greater than those considered here.

The most reliable research of an extensive character which has been carried out on the freezing-point lowerings of aqueous solutions is apparently that of Jahn.[2] He analyzed a portion of the solution in equilibrium with a large amount of ice after having determined the temperature, and he measured the latter independently by two mercury thermometers and in some cases also by the electromotive force at thermo-electric junctions. His results when plotted give regular curves, except in the case of lithium chloride, for which the curve is somewhat uncertain. A weight of either 5 or 4 has been ordinarily assigned to them except in the series in which the mercury thermometers alone were used, where a weight of 3 was assigned.

Results for the freezing-point lowerings of very dilute solutions of apparently high degree of accuracy have recently been published by Bedford.[3] Unfortunately the complete data are not yet available, the formal lowerings given by him being taken from a curve for a number of concentrations. This makes it difficult to judge the character of the results; but in view of the care and accuracy of the experimental work, a weight of 2 has been assigned.

A few series of results for single substances of considerable accuracy have been published. T. W. Richards,[4] using substantially the same method as Jahn, gives values at four concentrations for potassium chloride. A weight of 1 is given to these; for although the method was probably as accurate as Jahn's, few results are given, and temperatures were measured to 0.001° only. P. B. Lewis[5] also measured the freezing-point lowering caused by potassium chloride, reading his thermometer to 0.001°, using a large volume of solution, and introducing corrections for the ice separating and for pressure on the thermometer bulb. His results at practically four concentrations are given a weight of ½, since the point when plotted are too few and irregular to yield a reliable curve. The data obtained by Wildermann[6] for sulphuric acid have been included with a weight of unity. Of the freezing-point results published by Noyes and Johnston[7] only those for potassium ferrocyanide have been used, since the rest give either uncertain or improbable curves.

In two cases the results obtained in two independent series of experi-

---

[1] *Z. physik. Chem.*, 40, 185 (1902).

[2] *Ibid.*, 50, 129 (1904); 59, 31 (1907).

[3] *Proc. Royal. Soc.*, 83A, 454 (1910).

[4] *Z. physik. Chem.*, 44, 563 (1903).

[5] *J. Chem. Soc. (London)*, 95, 1 (1895).

[6] *Z. physik. Chem.*, 15, 350 (1894).

[7] THIS JOURNAL, 31, 1007 (1909).

TABLE 1—VALUES OF THE FORMAL FREEZING-POINT LOWERING.

Substance.	Observer.	Wt.	0.005	0.006	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
KCl	Jahn	5	...	3.618	3.594	3.558	3.503	3.451	3.391	3.352	...	...
	Jones	1	3.641	3.632	3.607	3.572	3.519	3.473	3.415	3.374	3.341	...
	Loomis	2	...	...	3.597	3.553	3.495	3.443	3.386	3.349	3.319	...
	Ponsot	½	...	...	...	...	...	3.421	3.406	3.394	3.373	...
	Abegg	1	...	...	3.650	3.569	3.432	...	...	...	...	...
	Hebb	3	3.664	3.656	3.633	3.596	3.534	...	...	...	...	...
	Raoult	1	...	...	...	3.504	3.462	3.426	3.388	3.364	3.346	3.331
	Richards	1	...	...	...	...	3.524	3.467	...	...	...	...
	Lewis	½	...	...	...	3.526	3.488	3.455	...	...	...	...
	Barnes	2	...	...	...	3.549	3.500	3.455	3.404	3.369	3.339	...
	Bedford	2	3.640	3.630	3.603	3.560	...	...	...	...	...	...
	Weighted mean		3.652	3.632	3.609	3.561	3.502	3.450	3.394	3.358	3.334	3.331
	Best value		3.648	3.640	3.610	3.564	3.502	3.451	3.394	3.359	3.334	3.314
	Mol number *i*		1.963	1.959	1.943	1.918	1.885	1.861	1.833	1.818	1.808	1.800
NH_4Cl	Loomis	2	...	...	3.565	3.531	3.480	3.435	3.387	3.359	...	...
	Jones	1	...	3.642	3.615	3.574	3.513	3.460	3.402	3.368	...	...
	Weighted mean		...	3.642	3.582	3.545	3.491	3.443	3.392	3.362	...	...
	Best value		3.617	3.608	3.582	3.544	3.489	3.442	3.392	3.362	...	...
	Mol number *i*		1.947	1.942	1.928	1.907	1.878	1.856	1.832	1.819	...	...
CsCl	Jahn	4	...	...	...	3.586	3.515	3.435	3.336	...	...	...
	Biltz	1	...	...		...		3.543	3.440	3.372	3.318	3.275
	Weighted mean		...	...	...	3.586	3.515	3.457	3.357	3.372	3.318	3.275
	Best value		...	...	...	3.586	3.515	3.454	3.385	3.339	3.304	3.275
	Mol number *i*		...	...	...	1.930	1.892	1.863	1.829	1.807	1.791	1.778
NaCl	Jahn	5	...	3.609	3.585	3.550	3.502	3.464	3.424	3.402	...	...
	Jones	1	3.656	3.645	3.616	3.575	3.518	3.470	3.416	3.381	3.356	3.336
	Loomis	2	...	...	3.619	3.577	3.517	3.466	3.413	...	...	...
	Hausrath, Osaka	1	...	...	3.639	3.600	...		...	...	...	...

	Raoult	½	.	.		. .	3.557	3.466	3.435	3.428	3.425	...
	Ponsot	1	.	.		..	..	.	3.411	3.404	3.398	...
	Barnes	2	...	..		3.583	3.538	3.498	3.447	3.412	3.384	...
	Weighted mean		3.656	3.615	3.602	3.568	3.516	3.472	3.425	3.407	3.386	3.336
	Best value		3.629	3.622	3.600	3.568	3.516	3.478	3.424	3.396	3.375	3.358
	Mol number *i*		1.953	1.949	1.938	1.922	1.892	1.875	1.850	1.838	1.830	1.824
LiCl	Jahn	4	3.611	3.608	3.600	3.582	3.550	3.515	. .	...	...	...
	Loomis	2	..	..	.	3.582	3.563	3.546	3.525	...	...	...
	Weighted mean		3.611	3.608	3.600	3.582	3.554	3.525	3.525	...	...	...
	Best value		3.612	3.609	3.598	3.582	3.553	3.525	. .	...	...	...
	Mol number *i*		1.944	1.942	1.937	1.928	1.912	1.901		...	..	...
NaBr	Jahn	3	...	..	...	3.611	3.551	3.507	3.463	3.437	...	...
	Mol number *i*		...	..	.	1.943	1.911	1.891	1.871	1.860	...	...
KBr	Jahn	3	..	..	...	..	3.490	3.437	3.389	3.363	...	...
	Biltz	1	...	.	..	.	3.567	3.509	3.447	3.408	3.380	3.357
	Weighted mean		.		.		3.509	3.455	3.404	3.374	3.380	3.357
	Best value		..	.	.	3.584[1]	3.509	3.455	3.404	3.374	3.352	3.337
	Mol number *i*		..	...	..	1.929	1.889	1.863	1.839	1.826	1.818	1.813
$NaNO_3$	Loomis	1	.		3.536	3.502	3.446	3.393	3.329	...	...	...
	Mol number *i*		.	.	1.903	1.885	1.855	1.830	1.798	...	...	...
KNO_3	Loomis	1	..	..	3.532	3.493	3.411	3.303	3.168	...	...	...
	Mol number *i*		. .	..	1.901	1.880	1.836	1.781	1.711	...	...	...
NH_4NO_3	Loomis	1	...	..	3.572	3.535	3.470	3.396	3.296	...	...	...
	Mol number *i*		..	..	1.922	1.903	1.868	1.831	1.780	..	...	...
$NaClO_3$	Jahn	3	...	..	..	3.523	3.506	3.450	.	...	...	...
	Mol number *i*		...	...	.	1.896	1.887	1.860	.	..	...	...

---

[1] The curves could be extended to 0.03 *N* from which this value was obtained by extrapolation.

TABLE 1—VALUES OF THE FORMAL FREEZING-POINT LOWERING—(*Continued*).

Substance.	Observer.	Wt.	0.005	0.006	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
$KClO_3$	Jahn	5	...	...	3.556	3.513	3.435	3.334	...	...	...	...
	Mol number *i*		...	...	1.914	1.891	1.849	1.798	...	...	...	...
$NaBrO_3$	Jahn	3	...	...	...	3.545	3.492	3.419	...	...	...	...
	Mol number *i*		..	...	...	1.908	1.879	1.844	..	..	...	...
$KBrO_3$	Jahn	5	...	...	3.573	3.524	3.445	3.348	..9	...	...	...
	Mol number *i*		...	...	1.923	1.896	1.854	1.805	...	...	...	...
$NaIO_3$	Jahn	5	3.603	3.592	3.560	3.512	3.423	3.289	.	...	...	...
	Mol number *i*		1.939	1.933	1.916	1.890	1.842	1.773	..	...	...	...
KIO_3	Jahn	5	3.606	3.593	3.555	3.497	3.397	3.274	...	...	...	...
	Mol number *i*		1.941	1.934	1.913	1.882	1.828	1.765	.	...	...	...
NaOH	Jones	1	3.719	3.706	3.654	3.495	3.408		...	...	...	...
	Mol number *i*		2.002	1.995	1.967	1.881	1.834	..	...	...	...	...
KOH	Jones	1	3.706	3.700	3.684	3.654	3.578	3.458	...	...	...	...
	Mol number *i*		1.995	1.991	1.983	1.967	1.926	1.865	...	...	...	...
HCl	Loomis	1	...	..	3.610	3.594	3.569	3.546	..	...	...	...
	Hausrath	1	...	...	3.683		.	.	..	...	...	...
	Jones	1	...	3.748	3.722	3.679	3.619	3.571	...	...	...	...
	Barnes	2	...	...	.	3.634	3.590	3.552	...	...	...	...
	Weighted mean		...	3.748	3.671	3.635	3.592	3.555	...	...	...	...
	Best value		3.700	3.692	3.669	3.637	3.591	3.555	...	...	...	...
	Mol number *i*		1.991	1.987	1.975	1.957	1.933	1.917	...	...	...	...
HNO_3	Loomis	2	...	...	..	3.560	3.508	3.480	3.459	...	...	...
	Jones	1	3.764	3.759	3.740	3.708	3.647	3.568	...	...	...	...
	Weighted mean		3.764	3.759	3.740	3.609	3.554	3.509	3.459	...	...	...
	Best value		3.667	3.661	3.642	3.609	3.552	3.524	3.478	...	...	...

	Mol number i		1.974	1.970	1.960	1.942	1.912	1.900	1.879	...	...	...
$KMnO_4$	Bedford	2	3.600	3.590	3.570	3.554		...	...	...	...	...
	Mol number i		1.938	1.932	1.921	1.913		...	...	...	...	...
Na_2SO_4	Loomis, Archibald	4	...	...		5.078	4.810	4.592	4.344	4.180	4.050	3.944
	Mol number i		...	...	...	2.733	2.589	2.472	2.344	2.257	2.190	2.134
K_2SO_4	Loomis	2		...	...	4.920	4.712	4.534	4.314	4.156	4.038	3.936
	Jones	1	5.352	5.326	5.244	5.108	4.870	4.624	4.310	...	...	...
	Abegg	1	...	...	...	4.876	...	...	...	...	...	...
	Archibald	2	...	...	...		4.772	4.594	4.340	4.176	4.058	3.964
	Osaka	2	5.288	5.260	5.178	5.024	...	...	...	...	...	...
	Ponsot	½	...	...	...		...	4.512	4.290	4.136	4.016	3.926
	Weighted mean		5.310	5.282	5.200	4.978	4.768	4.570	4.320	4.162	4.044	3.948
	Best value		5.308	5.282	5.198	5.040	4.776	4.568	4.324	4.162	4.044	3.948
	Mol number i		2.857	2.843	2.798	2.713	2.570	2.459	2.333	2.248	2.186	2.136
H_2SO_4	Loomis	2	...	...		4.480	4.256	4.100	3.950	3.868	3.812	3.770
	Ponsot	1		...	...	4.476	4.226	4.048	3.882	3.788	3.720	3.668
	Hausrath	1	5.144	5.100	4.964	4.764		...	...	...	...	...
	Jones	1	...		5.018	4.740	4.372	4.132	3.932	3.832	...	...
	Wildermann	1			4.782	4.524	4.242	4.072	3.928	3.856	3.812	...
	Barnes	2	...	...	...		4.376	4.164	3.972	3.876	...	...
	Bedford	2	5.008	4.928	4.752	4.624			...	...	...	...
	Weighted mean		5.050	4.985	4.854	4.580	4.300	4.112	3.940	3.852	3.790	3.736
	Best value		5.052	4.992	4.814	4.584	4.300	4.112	3.940	3.852	3.790	3.736
	Mol number i		2.719	2.687	2.591	2.467	2.316	2.216	2.125	2.080	2.047	2.022
$BaCl_2$	Bedford	2	5.182	5.158	5.092	5.000	...	...		...	...	...
	Loomis	1	...	...	...	5.076	4.858	4.750	4.676	4.644	4.628	...
	Jones	1	5.288	5.268	5.206	5.110	4.962	4.822	4.654	...	...	...
	Ponsot	1	...	...	5.062	5.004	4.898	4.786	4.648	4.560	...	...

TABLE 1—VALUES OF THE FORMAL FREEZING-POINT LOWERING—(*Continued*).

Substance.	Observer.	Wt.	0.005	0.006	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
	Weighted mean		5.217	5.191	5.113	5.038	4.906	4.786	4.660	4.602	4.628	...
	Best value		5.196	5.178	5.120	5.034	4.900	4.784	4.660	4.588	...	...
	Mol number *i*		2.797	2.787	2.756	2.709	2.637	2.575	2.515	2.479	...	...
$CaCl_2$	Loomis	1	...	...	...	5.140	4.974	4.876	4.792	..	...	...
	Ponsot	1	...	...	...	5.084	4.970	4.904	4.854	4.834	...	...
	Weighted mean		...	...	...	5.112	4.972	4.890	4.832	4.834	...	...
	Best value		...	...	...	5.112	4.966	4.886	4.832	4.810	...	...
	Mol number *i*		...	...	...	2.751	2.673	2.630	2.608	2.599	...	...
$SrCl_2$	Loomis	1	...	...	...	5.156	4.988	4.900	4.838	4.812	4.796	...
	Mol number *i*		...	...	...	2.775	2.685	2.637	2.611	2.600	2.595	...
$MgCl_2$	Loomis	1	...	...	...	5.144	5.032	4.974	4.938	...	...	...
	Mol number *i*		...	...	...	2.769	2.708	2.677	2.665	...	...	...
$ZnCl_2$	Jones	1	5.412	5.380	5.286	5.148	4.954	4.792	4.620	...	...	...
	Mol number *i*		2.913	2.896	2.845	2.771	2.666	2.579	2.493	...	...	...
$CdCl_2$	Jones	1	...	...	4.796	4.710	4.420	4.104	3.852	...	...	...
	Mol number *i*		...	...	2.581	2.535	2.379	2.209	2.078	...	...	...
$CdBr_2$	Jones	1	...	...	4.756	4.472	4.032	3.650	3.216	...	...	...
	Mol number *i*		...	..	2.560	2.407	2.170	1.964	1.734	...	...	...
CdI_2	Jones	1	...	...	4.062	3.864	3.344	2.694	2.266	...	...	...
	Mol number *i*		...	...	2.186	2.080	1.800	1.450	1.200	...	...	...
$Cd(NO_3)_2$	Jones	1	5.380	5.354	5.278	5.204	5.154	5.140	..	...	...	...
	Mol number *i*		2.896	2.882	2.841	2.801	2.774	2.767	...	...	...	...
$Ba(NO_3)_2$	Hausrath	1	5.264	5.236	5.156	5.034	...	...	...	...	...	..
	Mol number *i*		2.833	2.818	2.775	2.709	..	...	...	...	...	...

$Pb(NO_3)_2$	Hausrath	1	5.164	5.128	5.024	4.860	...	...	...	...	...	...
	Ponsot	1	...	...	...	...	4.448	4.220	3.960	3.756	3.560	3.428
	Weighted mean		5.164	5.128	5.024	4.860	4.448	4.220	3.960	3.756	3.560	3.428
	Best value		5.164	5.128	5.016	4.844	4.548	4.270	3.960	3.756	3.560	3.428
	Mol number *i*		2.779	2.760	2.700	2.607	2.448	2.298	2.136	2.028	1.923	1.854
$MgSO_4$	Loomis	2		...	...	2.654	2.514	2.382	2.236	2.140	2.070	2.008
	Hausrath	2	3.108	3.076	2.974	2.796	...	...	...	...	...	...
	Bedford	2	3.158	3.108	2.970	2.798	2.592		...	...	...	...
	Jones	1	...	3.300	3.212	3.078	2.864	2.640,	2.334	...	...	...
	Weighted mean		3.133	3.133	3.020	2.796	2.614	2.468	2.268	2.140	2.070	2.008
	Best value		3.148	3.112	3.006	2.854	2.638	2.460	2.270	2.156	2.074	2.008
	Mol number *i*		1.694	1.675	1.618	1.536	1.420	1.324	1.223	1.162	1.119	1.084
$NiSO_4$	Hausrath	2	3.220	3.192	3.036	2.832	...	...	...	...	...	...
	Mol number *i*		1.733	1.718	1.634	1.524	...	...	...		...	...
$ZnSO_4$	Hausrath	2	3.094	3.056	2.940	2.766	...	...	...	...	...	...
	Mol number *i*		1.665	1.645	1.582	1.489	...	...	...	...	...	...
$CdSO_4$	Hausrath	2	3.080	3.036	2.916	2.744	2.496		...		...	...
	Mol number *i*		1.658	1.634	1.569	1.477	1.343	...	...	...	...	...
$CuSO_4$	Hausrath	2	3.036	2.998	2.882	2.706	...	...	...	...	...	...
	Bedford	2	2.970	2.946	2.860	2.700	2.448	...	...	...	...	...
	Weighted mean		3.003	2.972	2.871	2.703	2.448	...	...	...	...	...
	Best value		3.003	2.972	2.871	2.703	2.448	...	...	...	...	...
	Mol number *i*		1.616	1.600	1.545	1.455	1.318	...	...	...	...	...
$K_3Fe(CN)_6$	Bedford	2	6.840	6.810	6.696	6.192	...		...	...	...	...
	Mol number *i*		3.681	3.665	3.604	3.333	...	...	...	...	...	...
$K_4Fe(CN)_6$	Noyes and Johnston	1	...	...	...	...	6.568	6.172	5.720	5.412	5.180	5.000
	Mol number *i*		...	...	...	...	3.535	3.322	3.079	2.913	2.796	2.700

ments by different observers have been plotted and combined in one curve. This has been done with Osaka's and Hausrath's results with sodium chloride, the individual experiments of the former showing a greater irregularity than those of the latter for this substance, although the same method was used by both; owing to the difficulty of drawing a satisfactory curve, a weight of 1 is given to the combined results. It has also been done with sodium sulphate, since the curves obtained from the data of Archibald and Loomis coincide; the final results are therefore given together, a weight of 4 being assigned to them.

Several other papers have been published in recent years presenting series of determinations of freezing-point lowerings extending up to very high concentrations. Only a few of the results in any of these series fall within the limits of concentration considered here; and they have, therefore, not been taken into consideration. In general, curves based upon only three or four results have been considered when the accuracy of the work justified their use or when more complete data are lacking.

Table I contains the separate values of the formal freezing-point lowering $\Delta t/N$ obtained by the various investigators and the means and best values derived from them in the way that has been described. The headings of the columns show the number of *equivalents* per 1000 grams water. The values of the mol number *i* given at the foot of each table were calculated by equation (4) of section 1.

3. Summary of the Mol Numbers Derived from the Freezing-point Lowerings.

The values of the mol number derived from the best values of the freezing-point lowering given in Table 1 are collected in Table 2. The concentrations, expressed in equivalents per 1000 grams of solvent, are shown at the heads of the columns. In the column headed "Wt." is given the sum of the weights assigned to the separate observations for each substance. These "weights" indicate roughly the relative probable accuracy of the mol numbers derived for the various substances, especially at the concentrations between 0.02 and 0.1 equivalents per liter.

TABLE 2 VALUES OF THE MOL NUMBER DERIVED FROM FREEZING-POINT LOWERINGS.

Subst.	Wt.	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
KCl	19	1.963	1.943	1.918	1.885	1.861	1.833	1.818	1.808	1.800
NH_4Cl	3	1.947	1.928	1.907	1.878	1.856	1.832	1.819	...	...
CsCl	5	...	...	1.930	1.892	1.863	1.829	1.807	1.791	1.778
NaCl	12½	1.953	1.938	1.922	1.892	1.875	1.850	1.838	1.830	1.824
LiCl	6	1.944	1.937	1.928	1.912	1.901	...	...	...	...
NaBr	3	...	...	1.943	1.911	1.891	1.871	1.860	...	...
KBr	4	...	...	1.929	1.889	1.863	1.839	1.826	1.818	1.813
$NaNO_3$	1	...	1.903	1.885	1.855	1.830	1.798	...	...	...
KNO_3	1	...	1.901	1.880	1.836	1.781	1.711	...	...	...

TABLE 2 (*Continued*).

Subst.	Wt.	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
NH_4NO_3	1	...	1.922	1.903	1.868	1.831	1.780	...	...	...
$NaClO_3$	3	...	...	1.896	1.887	1.860	...	...	...	...
$KClO_3$	5	...	1.914	1.891	1.849	1.798	...	...	...	...
$NaBrO_3$	3	..	...	1.908	1.879	1.844	...	...	...	...
$KBrO_3$	5	...	1.923	1.896	1.854	1.805	...	...	...	...
$NaIO_3$	5	1.939	1.916	1.890	1.842	1.773	...	..	...	...
KIO_3	5	1.941	1.913	1.882	1.828	1.765	..	...	...	...
$KMnO_4$	2	1.938	1.921	1.913		...	...	...	...	...
NaOH	1	2.002	1.967	1.881	1.834	...	. .	...	...	..
KOH	1	1.995	1.983	1.967	1.926	1.865	...	...	..	...
HCl	5	1.991	1.975	1.957	1.933	1.917	.	...	.	...
HNO_3	3	1.974	1.960	1.942	1.912	1.900	1.879	..	.	.
Na_2SO_4	4	..	.	2.733	2.589	2.472	2.344	2.257	2.190	2.134
K_2SO_4	8½	2.857	2.798	2.713	2.570	2.459	2.333	2.248	2.186	2.136
$BaCl_2$	5	2.797	2.756	2.709	2.637	2.575	2.515	2.479	..	..
$CaCl_2$	2	..	.	2.751	2.673	2.630	2.608	2.599	...	..
$SrCl_2$	1	..	..	2.775	2.685	2.637	2.611	2.600	2.595	...
$MgCl_2$	1	.		2.769	2.708	2.677	2.665	.		...
$ZnCl_2$	1	2.913	2.845	2.771	2.666	2.579	2.493	...		...
$CdCl_2$	1		2.581	2.535	2.379	2.209	2.078	..		...
$CdBr_2$	1	.	2.560	2.407	2.170	1.964	1.734	...	...	..
CdI_2	1	..	2.186	2.080	1.800	1.450	1.200	..	.	...
$Cd(NO_3)_2$	1	2.806	2.841	2.801	2.774	2.767	.	...	...	...
$Ba(NO_3)_2$	1	2.833	2.775	2.709		.		. .		..
$Pb(NO_3)_2$	2	2.779	2.700	2.607	2.448	2.298	2.136	2.028	1.923	1.854
H_2SO_4	10	2.719	2.591	2.467	2.316	2.216	2.125	2.080	2.047	2.022
$MgSO_4$	7	1.694	1.618	1.536	1.420	1.324	1.223	1.162	1.119	1.084
$NiSO_4$	2	1.733	1.634	1.524	. .	.	...	...	...	..
$CuSO_4$	4	1.616	1.545	1.455	1.318	..	.	...	...	...
$ZnSO_4$	2	1.665	1.582	1.489	...	..	..	...	...	...
$CdSO_4$	2	1.658	1.569	1.477	1.343	.	...	...	...	...
$K_3Fe(CN)_6$	2	3.681	3.604	3.333	...	...	...	..	...	...
$K_4Fe(CN)_6$	1	...	...		3.535	3.322	3.079	2.913	2.796	2.700

4. The Mol Number in Relation to the Type of Salt.

The salts of the uni-univalent type may be divided for convenience into the two groups represented by the general formulas MX and MXO_3. The former includes seven chlorides and bromides of the alkali elements. The mol numbers for these at any concentration show only comparatively small differences among themselves, excepting those for lithium chloride and sodium bromide at concentrations greater than 0.02. Excluding these, the mean mol numbers and their extreme values at the different concentrations are:

Concentration	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.4	0.5
Mean	1.952	1.937	1.925	1.887	1.864	1.837	1.823	1.812	1.804
Limits	1.944	1.928	1.907	1.878	1.856	1.829	1.807	1.791	1.778
	1.963	1.943	1.943	1.892	1.875	1.850	1.838	1.830	1.824

Except for the chlorides at the two lowest concentrations the values for the sodium salts are somewhat higher than those for the potassium salts. This is a general rule, as will be seen later. The values for potassium chloride and bromide agree throughout, with a maximum difference of 0.7 per cent. at the concentration 0.5; and those for cesium and ammonium chlorides agree very closely with those for potassium chloride except that the former decreases more rapidly in the more concentrated solutions. Sodium bromide shows at all the concentrations values about 1 per cent. greater than those for sodium chloride.

The mol numbers for the salts of the general formula MXO_3 are less than those for the salts of the formula MX at the same concentration with a few minor exceptions where they are practically identical. The values for the separate salts are scattered through a considerable interval, thus from 1.860 to 1.765 at 0.1 normal, so that a mean value would have little significance. The relations between the various salts are most clearly shown by arranging them in the way shown in the following table, in which the mol numbers at 0.1 normal are given:

	Cl.	ClO_3.	BrO.	IO_3.	NO_3.
Na...........	1.875	1 860	1.844	1.773	1.830
K............	1.861	1.798	1.805	1.765	1.781

It will be seen that the values for the sodium salts are always larger than those for the potassium salts; that those for the chlorates are nearly equal to those for the bromates, and that those for the nitrates are somewhat smaller, and those for the iodates much smaller, than these. It should be noted, however, that in the more dilute solutions (0.01 to 0.02 normal) the values for the iodates do not differ much from those for the other salts.

The mol numbers for potassium permanganate appear to approach more nearly those for the salts MX than those for the salts MXO_3 at the same concentrations.

The results for sodium and potassium hydroxide are probably somewhat too large; but even making some allowance for this the values appear to be greater than those for the salts MX. The latter is also true of hydrochloric and nitric acids, for which the final values are more accurate. The acid HX has furthermore greater i values than the acid HXO_3, in analogy with the salts of the types MX and MXO_3.

The unibivalent tri-ionic salts consist of the sulphates, halides, and nitrates.

The mol numbers for sodium and potassium sulphates differ from each other only to a slight extent (less than 1 per cent. throughout the total range of concentration), but those for the sodium salt are again slightly greater. The mean value is 2.465 at 0.1 normal and 2.723 at 0.02 normal.

With respect to the halides the following facts may be noted. Excluding the cadmium salts, all the values are of similar magnitude (the range being 2.57 to 2.68 at 0.1 normal and 2.71 to 2.77 at 0.02 normal), but are distinctly higher than those for potassium and sodium sulphates. The values for the cadmium halides are much less than those for the other halides, and decrease rapidly in the order chloride, bromide, iodide (namely at 0.1 normal from 2.21 to 1.96 to 1.45).

The three nitrates, of cadmium, barium, and lead, have mol numbers which differ greatly among themselves, those for lead nitrate (*e. g.*, 2.30 at 0.1 normal) being the smallest for any unibivalent salt, excepting the cadmium halides.

Bibivalent Salts.—Those investigated consist of the sulphates of five bivalent elements. The mol numbers do not differ greatly among themselves (1.46 to 1.54 at 0.02 normal); but are all much lower than those for the uni-univalent salts.

5. Change of the Mol Number with the Concentration.

The ionization of the various substances derivable from the mol number by equations (5) and (6) and the change in it with the concentration will be considered in a later article, after other properties from which it can be derived have been discussed. It is the purpose here only to show empirically the extent to which a simple cube-root formula corresponding to that which was found by Kohlrausch to express roughly the change in the equivalent conductance of certain types of salt with the concentration, will represent the change of the mol number with it. The cube-root formula of Kohlrausch $\Lambda_0 - \Lambda = K'C^{1/3}$, in which C is the concentration and K' a quantity constant for a given salt, assumes the form $1 - \gamma = KC^{1/3}$, if the conductance ratio Λ/Λ_0 be taken as a measure of the ionization γ, and if this equation be combined with (5) or (6), the following expressions result:

$$2 - i = K\,C^{1/3} \text{ for di-ionic salts} \qquad (8)$$

and

$$3 - i = 2K\,C^{1/3} \text{ for tri-ionic salts.} \qquad (9)$$

By means of these expressions the values of i have been calculated at various concentrations, assuming a value of K corresponding approximately to the observed i value at 0.05 or 0.1 normal, and comparing the so calculated values with the observed ones. For the sake of greater simplicity the mol numbers (by taking the mean) for such substances as have approximately equal mol numbers have been combined. The results are presented in Table 3 for those salts to which a total weight of 3 or more has been assigned and for which the experimental values extend over a sufficient range of concentration.

The observed and calculated values up to 0.1 normal agree almost completely in the case of the halides of the alkali elements; and they

TABLE 3—CHANGE OF THE MOL NUMBERS WITH THE CUBE-ROOT OF THE CONCENTRATION.

Substances.	K.	Conc.	0.005	0.01	0.02	0.05	0.1	0.2	0.5
MCl and MBr	0.292	Obs.	1.952	1.937	1.925	1.887	1.864	1.837	1.804
		Calc.	1.950	1.937	1.921	1.893	1.865	1.829	1.768
$NaClO_3$ and $NaBrO_3$	0.334	Obs.	...	...	1.902	1.883	1.852	...	...
		Calc.	..	..	1.909	1.877	1.845	...	...
$KClO_3$ and $KBrO_3$	0.418	Obs.	...	1.919	1.894	1.853	1.802	..	...
		Calc.	..	1.910	1.887	1.846	1.806	...	..
$NaIO_3$ and KIO_3	0.45	Obs.	1.940	1.915	1.886	1.835	1.769	..	..
		Calc.	1.923	1.903	1.878	1.834	1.791	...	...
Na_2SO_4 and K_2SO_4	1.10	Obs.	2.857	2.798	2.723	2.580	2.466	2.339	2.135
		Calc.	2.812	2.763	2.702	2.595	2.490	2.356	2.127
$BaCl_2$	1.00	Obs.	2.797	2.756	2.709	2.637	2.575	2.515	..
		Calc.	2.829	2.785	2.729	2.632	2.536	2.415	...
$Pb(NO_3)_2$	1.47	Obs.	2.779	2.700	2.607	2.448	2.298	2.136	1.854
		Calc.	2.749	2.684	2.602	2.459	2.318	2.140	1.833
$MgSO_4$	1.60	Obs.	1.694	1.618	1.536	1.420	1.324	1.223	1.084
		Calc.	1.726	1.655	1.566	1.411	1.258	1.064	...
$CuSO_4$	1.90	Obs.	1.616	1.545	1.455	1.318	..	..	.
		Calc.	1.675	1.592	1.485	1.301	...	...	..

differences not exceeding ½ per cent. in the case of the chlorates and bromates. In the case of the iodates and the tri-ionic salts, however, the differences at concentrations up to 0.1 normal frequently reach 1 per cent., but do not much exceed this. The bibivalent salts show deviations of several per cent., so that the principle can not be said to hold even approximately for them.

Attention may also be called to the fact that (since $K = -di/dC^{1/3}$) the value of the constant K furnishes an obvious measure of the relative rates at which the mol numbers of the various substances decrease with the increasing concentration. The regularities that exist will readily be seen by an examination of the values of K given in the table.

BOSTON, June, 1910.

SILVER NITRATE FORMED BY THE ACTION OF NITRIC ACID ON SILVER SULPHIDE.

BY HIPPOLYTE GRUENER.

Received May 30, 1910.

The statements which I have found concerning the products of the action of nitric acid on silver sulphide are incomplete and contradictory. The proportions of nitrate and sulphate formed vary widely with the conditions applied. Highly concentrated acid results in complete conversion to sulphate, while with the less concentrated acid there is formed a large percentage of nitrate. Besides concentration, temperature of the acid and time of action are influential.

In the experiments summarized in Table I, the precipitated sulphide

(0.2 g.) was treated with nitric acid (usually 15 g. of the pure acid) diluted to the proper concentration. The mixture was heated, or allowed to stand at the ordinary temperature. When the action had taken place, hot water was added to dissolve the nitrate and sulphate, the solution filtered from the sulphur and unchanged sulphide, and repeatedly evaporated to dryness. The amount of silver found in the residue determined the amount of sulphide dissolved. The nitrate formed was determined by the method of Gooch and Gruener.[1] The results are shown in Table I, which indicates the proportions of sulphide dissolved, and also the percentage of nitrate formed at different concentrations, *a*, with boiling acid, and *b* with cold acid.

TABLE I.

		a Acid boiling.			*b*. Acid cold		
No. of expt.	Conc. of HNO_3 Per cent	Time of action.	Per cent. Ag_2S dissolved.	Per cent. of possible nitrate formed	Time of action.	Per cent. Ag_2S dissolved	Per cent. of possible nitrate formed.
1.	94	50 min.	98.6	0	6 days	100	0
2.	71	5 min.	99.9	3.6	18 hours	95.0	7.2
3.	65	...	...	.	4 days	99.4	22.6
4.	55	10 min.	100	35.2	4 days	99.5	29.0
5.	45	3 min.	98.4	57.9	4 days	99.5	58.4
6.	35	3 min.	99.4	71.9	6 days	99.7	77.0
7.	25	5 min.	98.8	87.8	6 days	99.3	91.5
8.	20	until action was complete	98.9	94.7	11 days	98.6	95.9
9	15	until action was complete	98.9	90.9	11 days	98.8	97.0
10.	10	until action was complete	97.2	90.7	11 days	98.3	92.7
11.	7.5	15 min.	99.0	.	7 mos.	98.8	92.3
12.	5	30 min.	96.4	88.9	7 mos.	98.8	84.4
13.	2.5	4 hours	75.0	74.8	7 mos.	89.0	75.8
14.	1.25	20 hours	86.0	60.4	7 mos.	7.3	0

The complete conversion of the sulphide to sulphate by the strongest acid used suggests the other extreme, namely, complete conversion to nitrate. But the maximum formation of nitrate is found at about 20 per cent. acid, and with greater dilution the amount of nitrate is found to diminish. The advantage of the cold acid from the standpoint of the nitrate is apparent, for the average yield when the action takes place at ordinary temperature is about 10 per cent. greater than when the acid is heated.

The time of contact of the reacting substances is important. When the sulphur liberated by the first action is promptly removed, *i. e.*, by dilution and filtration, the percentage of nitrate is conspicuously greater than when longer contact is allowed. When the time of contact is lessened to increase the amount of nitrate, there is also a diminution of the amount of sulphide dissolved. These points are shown in Table II.

---

[1] *Am. J. Sci.*, 44, 117.

TABLE II.

HNO_3 = 71 per cent. Ag_2S = 0.2g.

Acid boiling				Acid cold.			
No. of expt.	Time of action.	Per cent. Ag_2S dissolved.	Per cent. nitrate formed.	No. of expt	Time of action.	Per cent. Ag_2S dissolved	Per cent. nitrate formed.
21	Heated just to boiling	62	39.5	31	1 hour	37.0	32.8
22	15 sec.	97.5	37.5	32	3.5 hrs.	53.6	20.8
23	30 sec.	96.6	21.1	33	9 hours	85.2	22.9
24	1 min.	91.4	8.4	34	18 hours	95	7.2
25	5 min.	99.7	3.6	35	42 hours	99.7	0.8
26	70 min.	100	1.1	36	66 hours	99.8	0.3

Summary.

Nitric acid, when of concentration above 5 per cent., dissolves precipitated silver sulphide rapidly. Very strong acid yields silver sulphate alone, while acid of lower concentration forms some nitrate in proportion to its dilution. 20–15 per cent. acid yields the maximum, about 95 per cent. nitrate, greater dilution again resulting in a smaller percentage. Heating the acid, or prolonging its time of action is unfavorable to the formation of nitrate.

CHEMICAL LABORATORY OF ADELBERT COLLEGE,
CLEVELAND.

GRAHAMITE, A SOLID NATIVE BITUMEN.

BY CLIFFORD RICHARDSON.

Received June 24, 1910.

Grahamite is a solid native bitumen, the type of which was first found in Ritchie County, West Virginia, in the early sixties of the last century. It was named for the Messrs. Graham, who were interested in the commercial development of the deposit, by Henry Wurtz. The early literature of the subject[1] is largely devoted to the origin of the material and to its relations to coal, asphalt and albertite, as the latter occurs in Nova Scotia.[2] It is largely controversial, which is not surprising in view of the fact that there had been little opportunity up to that time of studying and differentiating the native bitumens.

In 1890 Prof. Wm. P Blake, who had been interesting himself in the solid native bitumen found in such large amounts in veins in Utah and

---

[1] J. P. Leslie, *Proc. Am. Phil. Soc.*, **9**, 183 (1863). Henry Wurtz, *Am. J. Sci.*, [2] **42**, 420 (1865); *Proc. A. A. A. S.*, **18**, 124 (1869); *Am. Gas Light J.*, **11**, 98. S. F. Peckham, *Am. Gas Light J.*, **11**, 164 (1869). W. M. Fontaine, *Am. J. Sci.*, [3] **6**, 409 (1873). J. P. Kimball, *Am. J. Sci.*, [3] **12**, 277 (1876).

[2] Wetherill, *Trans. Am. Phil. Soc.*, 1852, 353.

Colorado, presented a paper[1] before the American Institute of Mining Engineers at its Washington meeting entitled "Uintaite, Albertite, Grahamite, and Asphaltum, Described and Compared with Observations on Bitumens and its Compounds," in which he stated, after reference to preceding papers, that the grahamite of West Virginia is neither albertite nor gilsonite (uintaite) but that all of these bitumens are plainly differentiated from each other by definite characteristics, although he relied on the statements of his predecessors for his characterization of grahamite. His conclusions, we shall see from the data which are to be presented, were entirely justified.

Grahamite attracted no further attention until 1899 when J. A. Taff, of the U. S. Geological Survey, published a paper[2] on "An Albertite-like Asphalt in the Choctaw Nation, Indian Territory," in which he describes a deposit of solid native bitumen occurring in the Impson Valley. Dr. Wm. C. Day, who examined it for him, concluded that it "resembled albertite more than any other asphaltic substance" though "the solubility in carbon disulphide classes the material with the asphalts rather than the coals." Dr. Day should have known that the albertite is practically insoluble in carbon disulphide and that, consequently, the material he had in hand could not be an albertite. He, like many other writers, had not had a sufficiently wide experience with the solid native bitumens to recognize their relations to each other and to identify them.

In 1901 a voluminous paper on "The Asphalt and Bituminous Rock Deposits of the United States," by George H. Eldridge, was published in Part I of the Twenty-second Annual Report of the U. S. Geological Survey. Most of the occurrences of grahamite came under his observation but, strangely enough, he failed to recognize the relations and similarity of any of them to the type grahamite of West Virginia. He went so far as to give the name "impsonite" to the grahamite found in the Impson Valley and writes of that found in Middle Park, Colorado, as asphalt. It is but fair to say that Mr. Eldridge, when his attention was called to the matter by the writer, after the appearance of his report, recognized the fact that many of the bitumens which he had described were, actually, as will be seen later, grahamites.

The confusion as regards bitumens of the three types, grahamite, albertite and gilsonite and also, to a limited extent, manjak continued.

In 1909 there appeared a Bulletin No. 380 of the U. S. Geological Survey "Contributions to Economic Geology" in which, under the heading "Asphalt" two papers appear, one, "An Occurrence of Asphaltite in Northeastern Nevada," by Robert Anderson, and another, "Grahamite Deposits of Southeastern Oklahoma," by Joseph A. Taff. Anderson undoubtedly uses the term asphaltite in the sense proposed by Eldridge in the classification of the native hydrocarbons and allied substances which he gives in his "Report," where he includes under asphaltites, albertite, impsonite, grahamite, nigrite and uintaite (gilsonite) although not distinguishing them from the true asphalts which do not appear in his table in any form. Anderson, no doubt, intends to convey the idea that the Nevada bitumen is not an asphalt. He says: "The asphaltite found here would be commercially known as 'grahamite' but its characteristics show it to differ from the variety so known scientifically. A few tests revealed a close relationship to the variety from Indian Territory described by G. H. Eldridge as impsonite." Anderson shows, therefore, that he is not aware that impsonite is grahamite. Taff's description of the solid bitumens of Oklahoma in the pages immediately following Anderson's paper shows that he is in accord with the ideas advanced by the writer some years ago[1] that many, if not all of the solid bitumens of Oklahoma are grahamites, taking that from West Virginia as a type.

---

[1] *Trans. Am. Inst. Min. Eng.*, 18, 563.

[2] *Am. J. Sci.*, [4] 8, 22

The confusion which has existed for many years as to what grahamite is becomes apparent from the preceding statement. It has arisen largely because no individual investigator has had in hand for comparison at one time, all of the very numerous deposits of solid native bitumen which are so widely distributed, particularly in North America and in the islands of the West Indies. Within the last fifteen years the writer has been so fortunate as to have referred to him specimens of nearly all the well-known occurrences of solid bitumen and of those which have been discovered during that period and was particularly fortunate in obtaining a large specimen of the original grahamite taken early in the seventies from the deposit in West Virginia, to which the name was originally applied and which must be regarded as the type. For this he is indebted to Prof. Charles F. Chandler, of Columbia University, whose identification of the material is, of course, authoritative.

In addition, specimens of this same bitumen, obtained when the vein was again worked for a short time in 1904–5 were available. The solid native bitumens which have been examined and which have the characteristics of grahamite are identified as to locality in the following list. Wherever possible reference is made to description of the deposits by geologists and others.

List of Occurrences of Grahamite.

WEST VIRGINIA.

No. 19,399 The type of material from Ritchie County, 25 miles a little north of east from Parkersburg, on McFarlan's Run near the South fork of Hughes River, taken from the vein at the time the mine was originally worked between 1868 and 1875. From the cabinet of Prof. C. F. Chandler.

---

[1] Report on the "Mineral Resources of Cuba in 1901," Gussenheimer, Weil & Co., not properly accredited to the author, and "The Modern Asphalt Pavement," John Wiley & Sons, N. Y. First edition, 1905, 203, second edition 1908, 211.

No. 75,637 From the Ritchie County deposit in 1904.

No. 75,673 10 ft. below No. 75,637 at the same time.

No. 82,088 From the Ritchie County deposit in 1905.

COLORADO.

No. 19,162 From the Middle Park deposit, Grand County, on Willow Creek, 21 miles from Grand River and 12 miles west of Grand Lake, 8 miles east of Park White Mt., 4 miles north of Grand Mt. S W. 15–6 and 22, T. 4 N. Range 77 West, specimen of 1898.

No. 19,260 Same.

No. 71,963 Same--Specimen of 1900.

No. 71,746 Same- Specimen of 1904.

OKLAHOMA.

No. 53,788 Impson Valley deposit, on a branch of Tenmile Creek, in the west side of Impson Valley near the south side of sec 21, T. 1 S, R 1 SE (Taff), specimen of 1901.

No. 74,989 Same shaft No 3, from "Old Slope," 24 ft depth, specimen of 1904.
No 74,990 Same shaft No. 3, from "Old Slope," 40 ft. depth, specimen of 1904.
No 74,991 Same shaft No 3, from "Old Slope," 70 ft depth, specimen of 1904.
No 74,992 Same shaft No 3, from "Old Slope," 90 ft. depth, specimen of 1904.
No 74,993 Same shaft No. 3, from "Old Slope," 110 ft. depth, specimen of 1904
No. 74,994 Same shaft No. 3, from "Old Slope," 135 ft. depth, specimen of 1904

No. 114,041 Same, from the stock of the Barber Asphalt Paving Company, Maurer, N. J. Four samples running from "A" with least luster to "D" with greatest luster, specimens of 1909.

No. 76,503 McGue Creek Valley deposit, Williams mine, on the west side of McGee Creek in the S. W. $^1/_4$ sec. 23, T. 1 N, R. 14 E. (Taff), specimen of 1905.

No. 76,504 Same.

No. 81,424 From the Choctaw Mining and Development Company, South McAlester, 1905.

No. 80,847 LeGrand's Stringtown deposit, in so-called "red bank" near Loco, Chickowaw Nation, Okla. This specimen is characterized by an infiltration of pyrite, in crystals readily recognized with the naked eye.

No. 59,398 Exact locality not known, 1902.

No. 80,824 From $2^1/_2$ miles southeast of Stringtown, Okla, at South edge of Boggy Creek Valley filling fissures in Ordovician or Silurian shales.

TEXAS.

Fayette County.
Webb County.

WYOMING.

No. 75,093 Locality not known, 1905.

MEXICO.

No. 12,113 Huasteca, Cristo deposit. The original material described by Kimball from the cabinet of Lehigh University.

No. 12,114 Same.

No. 64,152 From Victoria, 1903.

No. 83,982 From near the Eastern coast, 1905.

CENTRAL AMERICA.

No. 109,503 Unknown locality, 1909.

CUBA.

Pure bitumens.

No. 22,216 From "La America" mine near Bahia Honda, Province of Pinar del Rio, specimen of 1899.

No. 35,901 Same—Specimen.

No. 22,222 From "La Havana" mine near Campo Florida, Province of Havana, 1899.

No. 31,135 From an unidentified mine, twelve miles east of Havana, 1900.

Grahamites associated with mineral matter.

No. 21,415 From "Magdalena" mine, District of Mariel, Province of Pinar del Rio, Sample of 1899.

No. 21,657 Same.

No. 44,626 Same—Sample of 1901.

No. 52,000 Same—Sample of 1901.

No. 75,755 Same—Sample of 1905.

No. 21,416 From Mercedes mine, District of Mariel, Province of Pinar del Rio, 1899.

No. 25,131 From "Santa Eloisa" mine, near Santa Clara City, sample of 1899.

No. 47,617 Same—Sample of 1901.

No. 55,195 Same—Sample of 1901.

TRINIDAD, B. S. I.

No. 61,726–8 From Vistabella mine, near San Fernando, Trinidad, B. W. I., put on the market as "manjak," specimens of 1902.

No. 80,659 Same—Specimen of 1905.

METAMORPHOSED GRAHAMITES.

No. 69,235 Unknown locality, Oklahoma.

No. 69,482 From the Choctaw Mining and Development Company.

No. 69,242 Black Fork Mountain, Oklahoma.

Two samples.

(*a*) Near top of outcrop.

(*b*) Entry running in on vein from side of hill at a point probably 15 ft. below surface.

It will be seen from the number of occurrences mentioned in the preceding list that, if we are justified in considering them all as the same material, that is to say, as native bitumens corresponding to the type originally found in West Virginia, grahamite is very widely distributed.

The results of the examination of the specimens which have been studied are given in Table I.

In considering the data given some consideration must first be given to the subject of native bitumens in general and especially to the solid native bitumens from which grahamite is to be differentiated.

The native bitumens consist of a mixture of native hydrocarbons and small amounts of their nitrogen, sulphur and, in some cases oxygen derivatives, the character of any bitumen being dependent on that of the different series of hydrocarbons of which it is composed and their state of aggregation. Natural gas, petroleum in its various forms, maltha, asphalt, gilsonite, ozokerite and grahamite are bitumens, the four last being solids. They are all characterized by being soluble in carbon disulphide, but are differentiated by their physical and chemical characteristics. They all originate in petroleum and are products of metamorphosis, depending for their character on that of the petroleum from which they are derived and the environment to which this has been exposed during the last periods of time during which the changes have been going on. Petroleums are known to be of various types and include the paraffin oils of the Eastern states, which contain but a small amount of sulphur derivatives, the more sulphurous oils of the Ohio and Canadian type, which are largely made up of the paraffin series of hydrocarbons, the semi-asphaltic oils of Illinois, Texas and the mid-continental fields, varying in character as they are more or less asphaltic in nature, and the asphaltic oils of California, Mexico and the West Indies, which are practically free from paraffin hydrocarbons. As yet no petroleum of the Russian type has been found in the western hemisphere.

Solid bitumens are, apparently, formed from all of these types of petroleum. Ozokerite consists of solid paraffins and is plainly derived from paraffin petroleum. The type grahamite of West Virginia is found where paraffin petroleums alone are available as its source. That occurring in Middle Park, Colorado, must have had its origin in petroleum of the type found in that State at Florence, which is a paraffin oil. The grahamite of Oklahoma must have been derived from oil of the type of the mid-continental field which contains a large amount of paraffin hydrocarbons, although it is also asphaltic. All of the grahamites of the United States originate, therefore, in petroleums which are more or less of a paraffin nature. The contrary is the case with the grahamite of Trinidad, where the petroleum is purely asphaltic, as far as we know it to-day, but in appearance it can hardly be differentiated from that of the West Virginia deposit. The Cuban grahamites must, likewise, originate in asphaltic oils. These facts may prove of some value in differentiating the grahamites which have been examined.

From the non-paraffin oils are formed the asphalts, gilsonite, manjak and glance pitch, all of which have physical properties and chemical characteristics which differentiate them from one another and from grahamite. Before attempting to characterize grahamite, therefore, and to differentiate it from asphalt and the other solid bitumens something must be known in regard to these latter bitumens. Some data in regard to them are presented in Table II for comparison with which similar data in regard to the type grahamite from West Virginia are presented.

The native bitumens, it will be observed, are soluble in carbon disulphide. This is an essential characteristic. If the material is not soluble and, nevertheless, has been derived from petroleum it is regarded as a

TABLE I.

No.	Locality.	Fracture.	Luster.	Specific gravity.
19,399	West Virginia, 1870	Schistose or hackly	Dull	1.130
75,637	West Virginia, 1905	Schistose or hackly	Dull	1.137
75,673	West Virginia, 1905			1.121
82,088	West Virginia, 1905			..
19,162	Colorado, 1898	Schistose or hackly	Lustrous	1.160
19,260	Colorado, 1898	Schistose or hackly	Lustrous	1.159
31,963	Colorado, 1900	Schistose or hackly	Lustrous	1.152
71,746	Colorado, 1904			..
53,788	Impson Valley, Okla., 1901	Schistose or hackly	Lustrous	1.184
74,989	Impson Valley, Okla., 1904	Schistose or hackly		..
74,990	Impson Valley, Okla., 1904	Schistose or hackly		..
74,991	Impson Valley, Okla., 1904	Schistose or hackly		..
74,992	Impson Valley, Okla., 1904	Schistose or hackly		..
74,993	Impson Valley, Okla., 1904	Schistose or hackly		..
74,994	Impson Valley, Okla., 1904	Schistose or hackly		..
114,041*a*	Impson Valley, Okla., 1909	Schistose or hackly	Very dull	..
" *b*	Impson Valley, Okla., 1909		Dull	..
" *c*	Impson Valley, Okla., 1909		Sub-lustrous	..
" *d*	Impson Valley, Okla., 1909		Lustrous	..
76,503	McGee Creek, Okla., 1905	Schistose or hackly	Sub-lustrous	..
76,504	McGee Creek, Okla., 1905	Schistose or hackly	Lustrous	..
81,424	South McAlester, Okla., 1905	Schistose or hackly	Lustrous	..
80,824	Stringtown, Okla., 1905	Schistose or hackly	Sub-lustrous	..
64,847	LeGrand, deposit, Okla., 1903	Schistose or hackly	Dull	..
59,398	Unknown, Okla., 1902	Schistose or hackly		..
	Fayette Co., Texas, 1909			..
	Webb Co., Texas, 1909			..
75,093	Wyoming, unknown, 1901			..
	MEXICO.			
64,152	Victoria, 1903			..
83,982	Near Eastern Coast, 1905	Smooth, semi-conchoidal	Lustrous	..
12,113	Huasteca, 1876			1.145
12,114	Huasteca, 1876			..
	CENTRAL AMERICA.			
109,503	Unknown locality, 1909			..
	CUBA.			
22,216	Bahia Honda, "La America" mine, 1899	Distinct cleavage, thin layers	Semi-bright, coal like	1.157
35,901	Bahia Honda, "La America" mine, 1900	Distinct cleavage, thin layers	Semi-bright, coal like	1.235
22,222	Campo Florida, "La Havana mine," 1899	Smooth, semi-conchoidal	Dull	1.175
31,135	Unidentified mine, 12 m E. Havana, 1900	Smooth, semi-conchoidal	Dull	1.163
21,415	Mariel, "Magdalena" mine, 1899	Conchoidal	Dull	1.444
21,657	Mariel, "Magdalena" mine, 1899	Conchoidal	Dull	1.409
44,626	Mariel, "Magdalena" mine, 1901	Conchoidal	Dull	1.460
52,000	Mariel, "Magdalena" mine, 1901	Conchoidal	Dull	1.4341
75,755	Mariel, "Magdalena" mine, 1905			..
21,416	Mariel, "Mercedes" mine, 1899	Conchoidal	Dull	1.562
25,131	Santa Clara, "Santa Eloisa" mine, 1904	Smooth, semi-conchoidal	Lustrous	1.2735
47,617	Santa Clara, "Santa Eloisa" mine, 1905	Smooth, semi-conchoidal	Lustrous	1.2935
55,195	Santa Clara, "Santa Eloisa" mine, 1901	Smooth, semi-conchoidal	Lustrous	1.2859
	TRINIDAD.			
61,726	Vistabella "Manjak," 1902		Dull	..
61,727	Vistabella "Manjak," 1902		Lustrous	..
61,728	Vistabella "Manjak," 1902		Bright	..
80,659	Vistabella "Manjak," 1905			1.156
	METAMORPHOSED OR ALTERED GRAHAMITES.			
69,235	Unknown locality, Okla., 1904			..
69,482	South McAlester, Okla., 1904			..
6[illegible]242*a*	Black Fork Mountain, Okla., 1904	Schistose	Sub-lustrous	..
[illegible] *b*	Black Fork Mountain, Okla., 1904	Schistose	Sub-lustrous	..

[1] Contains pyrite.

Loss 100°.	Bitumen.	Inorganic matter.	Difference.	Per cent. of total bitumen soluble in naphtha.		Bitumen ins. CCl_4.	Bitumen ins. hot turpentine.	Residual coke.	Ultimate composition of pure bitumen.				Diff.	Test No.
				88° B.	62° B.				C.	H.	S.	N.		
0.4%	97.7%	2.0%	0.3%	9.4%	10.7%	..	..	36.8%	86.56%	8.68%	1.79%	..	2.97%	19,399
0.0	97.8	2.1	0.1	3.4	3.5	55.0	0.8	40.1	...	..	..	..	...	75,637
...	97.6	1.9	0.5	1.4	2.7	..	..	39.7	..	..	..	..	...	75,673
0.4	..	1.8	..	..	..	..	..	41.4	..	..	..	..	...	82,088
...	98.2	0.1	1.7	0.8	..	80.6	..	47.4	85.97	7.65	0.93	..	5.45	19,162
...	99.0	0.1	0.9	..	..	..	..	48.4	86.08	7.63	0.95	..	5.34	19,260
...	98.7	trace	1.3	1.3	1.3	.	..	48.3	85.90	7.75	0.99	..	5.36	31,963
0.7	99.3	0.1	0.6	0.9	1.0	..	..	49.3	...	..	..	..	...	71,746
0.4	90.5	1.1	8.4	0.8	1.1	..	..	56.4	...	..	..	..	...	53,788
...	96.2	3.0	0.8	0.7	.	..	..	52.9	83.90	7.14	2.24	..	6.72	74,989
...	95.7	4.1	0.2	0.4	..	..	..	51.4	...	..	..	..	...	74,990
...	95.5	4.2	0.3	0.2	..	..	..	52.6	...	..	..	..	...	74,991
...	95.2	3.9	0.9	0.7	..	..	.	52.9	...	..	.	..	...	74,992
...	93.5	5.0	1.5	0.7	..	..	..	52.0	...	..	..	..	..	74,993
...	93.0	5.3	1.7	0.7	.	..	..	52.0	...	..	..	..	...	74,994
0.1	92.4	6.6	1.0	..	..	..	43.0	49.1	..	..	1.04	..	...	114,041a
0.1	95.4	3.8	0.8	..	..	..	..	51.1	..	..	1.56	..	...	" b
0.0	94.0	6.0	0.0	..	..	..	..	49.1	..	..	1.52	..	..	" c
0.2	93.3	6.7	6.0	..	..	..	..	48.5	...	..	1.40	..	...	" d
..	99.7	0.3	0.0	6.8	8.2	..	..	43.5	..	..	..	..	...	76,503
..	95.7	0.3	4.0	4.5	5.4	..	..	45.7	..	..	..	..	...	76,504
..	99.4	0.6	0.0	6.8	.	58.2	..	44.0	.	.	..	..	..	81,424
0.7	83.7	7.1	9.2	5.0	..	37.9	.	41.0	..	..	..	..	...	80,824
0.6	76.4	23.6[1]	0.0	6.3	7.5	..		39.4	...	..	..	..	..	64,847
..	96.8	2.6	0.6	0.9	1.0	..	..	54.0	...	..	..	..	...	59,398
0.3	..	4.2	..	..	..	..	..	37.7	76.2	6.6	7.4	0.4	5.2	....
0.3	..	2.9	..	..	..	..	..	52.8	78.6	7.5	5.4	1.2	5.1	....
..	99.0	..	0.8	0.5	..	..	..	51.2	..	..	..	..	...	75,093
..	..	3.4	..	..	..	..	..	54.0	...	..	...	..	...	64,152
..	..	2.8	..	..	..	..	..	38.0	...	..	..	..	...	83,982
..	93.8	2.8	3.4	8.4	..	..	40.5	35.3	83.14	8.09	5.47	..	...	12,113
..	..	..	..	..		..	..	..	77.67	8.06	7.51	..	...	12,114
..	25.6	0.4	74.0	38.1	..	12.2	..	43.2	...	..	..	..	...	109,503
0.4	99.4	0.5	0.1	20.0	38.8	24.3	9.8	40.0	81.94	7.45	7.65	..	2.96	22,216
0.2	99.6	0.4	0.0	17.4	22.2	0.9	0.3	42.2	81.28	7.17	6.23	..	5.32	35,901
0.1	98.9	0.4	0.7	6.0	22.5	..	..	45.0	82.53	7.47	6.42	..	3.58	22,222
0.2	99.2	0.5	0.3	11.3	12.6	..	..	44.0	...	..	..	..	...	31,135
2.8	58.1	41.2	0.7	37.7	53.5	2.2	6.4	36.0	77.82	8.69	6.86	..	6.63	21,415
2.0	58.0	38.1	3.9	40.2	55.9	1.5	6.8	38.2	74.13	8.58	7.59	..	9.70	21,657
3.8	54.8	39.9	5.3	39.8	48.5	2.0	7.6	33.6	72.49	8.45	7.68	..	11.38	44,626
3.0	58.2	37.9	3.9	48.2	57.3	6.3	10.6	26.9	...	..	..	..	...	52,000
..	58.0	38.3	3.7	..	..	..	..	22.3	...	..	..	..	...	75,755
3.6	49.8	48.4	1.8	42.3	55.0	..	4.3	37.4	75.91	7.81	7.81	..	8.48	21,416
0.8	79.1	19.1	1.8	..	47.1	2.0	19.1	35.0	82.43	6.99	8.72	..	...	25,131
2.5	77.4	20.4	2.2	..	39.7	2.7	19.0	34.0	...	..	..	..	...	47,617
..	77.8	20.0	2.2	..	43.7	2.9	11.4	34.9	...	..	..	..	...	55,195
0.2	97.5	2.5	0.0	14.8	15.2	..	..	40.0	...	..	..	..	...	61,726
0.2	98.8	1.2	0.0	12.4	13.2	..	..	35.0	...	..	..	..	...	61,727
0.3	91.5	4.9	0.0	14.5	18.2	..	..	33.0	...	..	..	..	...	61,728
..	94.2	5.8	trace	19.2	..	38.8	..	31.0	83.95	5.66	3.83	2.24	...	80,859
0.5	41.6	0.03	58.1	8.4	8.9	..	..	48.0	...	..	..	..	...	69,235
..	41.1	0.2	58.7	..	..	..	..	47.0	...	..	..	..	...	69,482
1.6	3.6	3.3	93.1	0.0	0.0	..	..	75.0	...	..	..	..	...	69,242a
0.3	2.6	0.6	96.8	0.0	0.0	..	..	77.0	...	..	..	..	...	" b

TABLE II.

Test No.	W. Va. Grahamite. 75,637.	Campo Florida, Cuba. Grahamite. 22,222.	Nova Scotia. Albertite. 7,834.	Egypt. Glance pitch. 14,145.	Barbadoes. Manjak. 14,144.	Utah. Gilsonite. 68,941	Lake Asphalt. Dry Trinidad. 63,260	Wurtzelite. 72,684.	Ozokerite.
Physical Properties.									
Sp. gr. 25°/25° original substance........	1.137	1.175	1.075	1.097	1.100	1.0433	1.40	1.064	——
Streak..............................	Black	Brownish-black	Black	Black	Black	Red-brown	Blue-black	Black	Brown-black
Lustre..............................	Dull	Dull	Lustrous	Lustrous	Lustrous	Lustrous	Dull	Lustrous	Dull
Structure............................	Fractured	——	Uniform	Uniform	Uniform	Uniform	Homogeneous	Uniform	Paraffin
Fracture............................	Hackly	Semi-conchoidal	Conchoidal	Conchoidal	Conchoidal	Conchoidal	Semi-conchoidal	Conchoidal	Irregular
Flows...............................	Intumesces	Intumesces	Intumesces	127° C.	221° C.	152° C.	88° C.	Intumesces	72° C.
Chemical Characteristics.									
Bitumen soluble in CS_2, air temperature..	97.8%	98.9%	5.9%	99.7%	98.3%	99.4%	56.4%	6.7	100.0
Difference...........................	0.1	0.7	94.1	0.2	0.5	0.3	6.4	92.5	0.0
Inorganic or mineral matter.............	2.1	0.4	0.0	0.1	1.2	0.3	36.9	0.8	trace
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Malthenes.									
Bitumen soluble in 88° naphtha, air temp.	3.3%	...	1.5%	23.5%	22.2%	53.9%	35.6%	...	...
This is per cent. of total bitumen.........	3.37	6.0%	..	23.6	23.6	54.2	63.1	0.0	94.1
Carbenes.									
Bitumen insoluble in CCl_4, air temperature, bitumen yields on ignition	55.0%	...	..	0.1%	1.2%	0.5%	1.3%	...	...
Residual coke.........................	41.0%	45.0%	29.8%	15.0%	24.7%	14.5%	10.8%	8.3	0.0
Ultimate Composition.									
Carbon..............................	86.56%	82.53%	83.44	80.87	89.95	89.28	82.33	80.00	85.25
Hydrogen............................	8.68	7.47	10.08	10.42	9.04	8.66	10.69	12.33	15.09
Sulphur.............................	1.79	6.42	0.44	8.52	0.73	1.79	6.56	5.83	0.00
Difference...........................	2.97	3.58	6.04	0.19	0.28	0.79	0.82	1.84	0.00

pyrobitumen. Such a material is represented in the table by albertite. This may be regarded as a bitumen in which the metamorphosis, beginning in petroleum and extending through maltha, asphalt and grahamite, has terminated in a material which is no longer soluble. On this ground grahamite is an intermediate material between asphalt and albertite. The extent of the metamorphism may be measured, it will be observed, by a comparison of the relative solubility of the bitumens in light petroleum distillates, and in the heavy petroleum residuals, known as fluxes, by the amount of residual coke which they yield on ignition and to a certain extent by their density and melting points. For this purpose data in regard to bitumens of the series extending from petroleums which are mobile liquids to grahamite and albertite are here presented.

				Solubility in			
						heavy residuals	
	Spec grav.	Melting point.	Residual coke	carbon disulphide.	light naphtha	paraffin.	asphaltic.
Paraffin petroleum	0.83	liquid	0.0	100.0	100.0	.....	.....
Asphaltic petroleum	0.93	liquid	1.0	100.0	98.0	...	.....
Maltha	0.99	viscous	3.0	98.0	94.0	...	....
Asphalt, medium	1.03	60°	12.5	96.0	70.0	homogenous	......
Asphalt, hard	1.04	80°	14.5	...	63.0	homogenous	......
Gilsonite	1.04	130°	15.0	99.4	53.0	non-hom.	homogenous
Glance pitch	1.10	130°	15.0	99.7	23.5	non-hom.	homogenous
Manjak	1.10	200°	24.7	98.3	22.2	non hom.	homogenous
Grahamite, Trinidad	1.16	intum.	35.0	98.8	14.5	non-hom.	homogenous
" West Va	1.14	intum	41.0	97.8	3.3	non-hom.	homogenous
" Oklahoma	1.18	intum	56.4	95.5	0.8	non-hom.	homogenous
Albertite	1.08	intum	29.8	6.0	1.5	insol	insol.

The preceding data present a fairly regular rate of metamorphism from petroleum to grahamite and illustrate very well the relation of grahamite to the other native bitumens, as well as the justification for its differentiation from asphalt and gilsonite. Grahamite does not melt. Asphalt, gilsonite and glance pitch become liquid on the application of heat. Grahamite is but slightly soluble in naphtha, whereas the other solid bitumens contain a considerable percentage which is soluble, corresponding in amount to the degree to which they have been metamorphosed. The grahamites yield a higher percentage of residual coke, this too corresponding to the extent of the metamorphism. The density of this form of bitumen is greater than that of the bitumens which melt readily.

Grahamite in its outward physical appearance is as a rule, and where it is not associated with mineral matter, characterized by a peculiar structure and fracture, which is found in no other form of solid native bitumen. While the material is homogenous or uniform as far as composition is concerned for any one specimen, the fracture is not conchoidal or that of a homogeneous solid such as gilsonite, glance pitch, manjak or the pure asphalts. On the contrary it presents a surface which shows that the bitumen has been subjected to pressure and to motion from movement of the vein walls which it is too brittle to resist. The result has been a fine fracture carried entirely through the mass, which results in a surface, when grahamite is broken, which is more or less schistose in structure. It has been described as hackly and also termed pencillate. It is found in all the grahamites occurring in the United States, in that from Trinidad and in the pure bitumens from Cuba. The deposit at Huasteca, Mexico, has a lustrous fracture like that of glance pitch while in some of the grahamites of Cuba the fracture is masked by the high percentage of mineral matter which is present.

In powder, grahamite, like asphalt and glance pitch, is black and it gives a black streak. This differentiates it sharply from gilsonite, which yields a light brown powder.

It does not melt readily, as has been said, and this alone differentiates it from all the other bitumens and justifies us in putting all the grahamites in a class by themselves. It intumesces and swells up at high temperatures with the evolution of gas, but softens to some extent so that it can be in part drawn out into threads. In this respect it resembles the pyro-bitumen albertite, although it differs entirely from it by its solubility in carbon disulphide.

In their ultimate composition the grahamites show some interesting differences from the other solid bitumens and among themselves, which are of importance and without which any consideration of this form of bitumen would be incomplete.

An ultimate analysis by combustion of the grahamite from West Virginia shows that it consists of

C, 86.56; H, 8.68; S, 1.79; undetermined, 2.97,

the preceding figures being calculated on a basis of bitumen free from mineral matter. For comparison with these figures data in regard to the ultimate composition of three well-known asphalts will serve.

	Pure bitumens. Trinidad.	Pure bitumens. Bermudez.	Waldorf, Cal.
Carbon	82.33	82.88	82.77
Hydrogen	10.69	10.79	10.62
Sulphur	6.16	5.87	6.47
Nitrogen	0.82	0.75	0.35
	100.00	100.29	100.21

The West Virginia grahamite differs from asphalt by containing a much smaller amount of sulphur derivatives, more carbon and less hydrogen. The relation of carbon to hydrogen, considering sulphur as an equivalent to two atoms of hydrogen, is as follows:

	Grahamite.	Asphalt.
Carbon	90.9	88.5
Hydrogen	9 1	11.5
	100.0	100.0

This relation and the presence of the larger amount of carbon may be regarded as explaining, to a certain extent, the differences between the two forms of bitumen as well as the larger yield of residual coke from grahamite and the fact that it does not melt readily.

Having shown the characteristics of the type grahamite, the next step is the differentiation of the various other deposits on the basis of their behavior with certain solvents, their purity or admixture with mineral matter and their ultimate composition; this with a view of determining whether they may all be properly included under the one designation "grahamite," whether they should be separated into classes, or whether specific names should be applied to some of the bitumens as has been done by some writers who were not familiar enough with the native solid bitumens to recognize grahamite when it was met in a new locality. Of course, in so doing, the material from West Virginia which was described in the early sixties of the last century must serve as the type.

This, it appears, contains 86.6 per cent. of carbon and 1.8 per cent. of sulphur. Some of the other grahamites have a similar ultimate composition, notably those from Middle Park, Colorado, and various localities in Oklahoma. The carbon in these occurrences lies within the extremes, 86.6 and 83.9, the latter figure for the Impson Valley material which was called impsonite by Eldridge. This approaches the amount found in asphalt and is smaller by 2.7 per cent. than the carbon in the type grahamite.

It is questionable whether this is sufficient to authorize a specific name, especially in view of the fact that the two materials in other respects are so strikingly alike, in their fracture and general appearance, in not melting and in their insolubility in light naphtha and dense paraffin residuums. From the writer's point of view the West Virginia, Colorado and Oklahoma bitumens may safely be recognized as all being grahamites.

So closely allied to these three occurrences that it cannot be distinguished from them in external appearance is the grahamite of Trinidad. It has the same hackly fracture as the type material, does not melt or flux smoothly with the paraffin oils, yields from 31 to 40 per cent. of residual coke and is readily recognized by the trained eye as a grahamite. It differs from the bitumen of this type as found in the United States only by the presence of nitrogen to the extent of over 2 per cent., in which it is unique, a higher percentage of sulphur, 3.83 as compared to 1.79, and its considerably greater solubility in light naphtha, 13.0–15.0 per cent. as compared with fractions of a per cent. in the Colorado and Oklahoma material and 1.4 to 9.4 in the original grahamite from West Virginia, the higher figure in the latter case being for the product of the operations in the sixties and the latter for material taken out in recent years. Further, the two materials differ in a marked degree in ultimate composition, as far as the percentages of carbon and hydrogen are concerned, the Trinidad grahamite containing but five per cent. of hydrogen whereas the West Virginia carries nine, and only 84 per cent. of carbon as compared with 86.5.

	West Va.	Trinidad.
Carbon	86.56	83.95
Hydrogen	8.68	5.66
Sulphur	1.79	3.83
Nitrogen	...	2.24
Difference	2.97	4.32

It may be held that the Trinidad bitumen differs sufficiently from the type grahamite to make it a distinct form, but the difference can be readily explained by the different character of the two petroleums from which the two deposits have been derived, the West Virginia grahamite originating in a paraffin oil and that from Trinidad in an asphaltic one. It is possible that grahamite must be considered as a class of bitumens, rather than a species, or genus, and this will be further confirmed as the characteristics of the other individual deposits are examined. There seems to be no reason, however, why the Trinidad bitumen should not be regarded as a grahamite. It is certainly not a manjak, although it has been put upon the market as such; a manjak being a bitumen which has a smooth fracture like glance pitch and melting readily. The comparatively high percentage of residual coke which manjak yields does, however, show that it is a material which, in its metamorphism, is somewhat related to grahamite. In this connection it is worthy of note that in Barbadoes, where alone manjak occurs, a continuous series of bitumens is found ranging from maltha to one of the hardest consistency.

If we look further into the ultimate composition of the remaining grahamites which have been examined, it is seen that they all contain more sulphur than those which we have had under consideration, from 5.4 to 8.7 per cent. as compared with 0.93 to 3.83 per cent. It is possible, therefore, to divide the grahamites into two classes, those containing less than four per cent. and those having more than five per cent. of sulphur. The presence of sulphur may be attributed in part to sulphur derivatives of hydrocarbons existing in the original oils from which the grahamites are derived, but we know of no petroleums which contain a sufficient amount of such components to account for the high percentage of sulphur found in the second class of grahamites. The assumption that this might be accounted for by concentration due to evaporation during the long period during which the metamorphosis has gone on will not serve, since this change has taken place, if we may judge from the location of the deposits, under conditions where volatilization could not occur, so that it must be adventitious in most, if not in all cases. The bitumen of Trinidad asphalt, however, contains 6.5 per cent. of sulphur and this may be considered as the source of grahamite of that island and of that of the sulphur which it carries, as the two bitumens are found not far apart. The bitumen of the asphalt, on the other hand, is associated with an asphaltic petroleum, issuing from wells sunk immediately adjoining the deposit, which contains only about 1.5 per cent. of sulphur. It is difficult, therefore, to say definitely what the source of the sulphur in grahamite is, but it must be in certain cases adventitious, as the bitumen found at the Le Grand deposit in Oklahoma contains quite large and well defined crystals of pyrite, visible to the naked eye, which have been deposited by infiltration through the fractures of the material.

In Cuba deposits of bitumen are found which carry a very considerable amount of adventitious earthy matter, resembling in this respect Trinidad asphalt, but the characteristics of the bitumens are such that they may be considered as grahamites, since these yield a high percentage of residual coke, over 30 per cent., and have a high density, although they are, like the Trinidad grahamite, more soluble in light naphtha than the type grahamite and, possibly, should be classed by themselves on this account, and because of their peculiar ultimate composition, as they contain, in addition to a high percentage of sulphur, much organic matter the nature of which is not revealed in the ordinary methods of combustion and which may be oxygen.

Very pure grahamites are also found in Cuba at Bahia Hondo and Campo Florida, equalling in this respect those from West Virginia, Colorado and Oklahoma, and differing from them only in their higher percentage of sulphur and greater solubility in light naphtha. The Bahia Honda bitumen resembles in outward appearance the type grahamite, having the schistose or hackly fracture.

The grahamite from Huasteca, Mexico, described by Kimball[1] is a unique one in that it resembles gilsonite in its high lustre and fracture and in that it melts. It is quite insoluble in light naphtha, however, yields a high residual coke and corresponds in ultimate composition with grahamite. Kimball seems, therefore, to have been justified in classing it as such.

In this connection it is not out of place to call attention to the resemblance of grahamite to that portion of the bitumen of the asphalts which is soluble in carbon disulphide but insoluble in light naphtha and which has been defined as a class as "asphaltenes" by the writer in distinction from the more soluble form which has been termed "malthenes" from their resemblance to natural maltha. The asphaltenes, like grahamite, do not melt, are not soluble in light naphtha, yield a high residual coke and have a similar ultimate composition, as can be seen from the following data:

---

[1] *Am. J. Sci.*, [3] 12, 277 (1876).

	Trinidad asphalt Asphaltenes.	Grahamite Bahia Honda.	Bermudez asphalt Asphaltenes	West Va. Grahamite
Specific gravity	1.121	1.157	1.110	1.130
Residual coke	32.00	40.00	37.00	36.80
Carbon	82.01	81.94	87.19	86.56
Hydrogen	7.82	7.45	8.47	8.68
Sulphur	10.86	7.65	4.83	1.79
Difference	...	2.96	..	2.97
	100.69	100.00	100.49	100.00

The agreement in the ultimate composition, specific gravity and yield of residual coke between the asphaltenes in the asphalts and the grahamites which contain larger and smaller amounts of sulphur is striking, and is evidence of the gradual metamorphosis of petroleum into grahamite.

In the table of analyses of grahamites data are given of several materials from Oklahoma under the heading "metamorphosed or altered grahamites." These are distinguished by their smaller solubility in carbon disulphide than that of the grahamites. They illustrate the intermediate stages between that bitumen and the pyrobitumens such as albertite and the transition of one form into the other, although it has not been positively shown that the type albertite, from Nova Scotia, is derived from petroleum, as are the solid native bitumens which have been described in this paper. There is a great probability that it is a type of coal.

The behavior of the grahamites with other solvents than those which have been mentioned is also of interest. Oil of turpentine and carbon tetrachloride do not have the same solvent power with all of them. In studying the solvent power of the former on various bitumens it was found that it dissolved when cold but 0.8 per cent. of the bitumen in the grahamite from the Impson Valley, 4.8 in that from West Virginia, and in all the others but little, as on standing in contact with them for twelve hours it was practically uncolored. With gradual rise in temperature the action was not increased and no solution takes place until the boiling point of the turpentine is nearly reached, when at a definite point the bitumen dissolves. On cooling the bitumen separates out. The amount dissolved at high temperatures varies, as can be seen in the following table:

SOLUBILITY OF GRAHAMITES IN HOT OIL OF TURPENTINE.

		Solubility in		Per cent. of total bitumen sol. in turp
		hot turpentine	carbon disulphide.	
35,901	Bahia Honda, Cuba	99.3	99.6	99.7
75,637	West Virginia	96.9	97.8	99.1
21,416	Mercedes Mine, Cuba	46.3	49.6	93.3
22,216	Bahia Honda, Cuba	89.6	99.4	90.1
21,657	Magdalena Mine, Cuba	51.2	58.0	88.2
44,626	Magdalena Mine, Cuba	47.2	54.8	86.1
55,195	Santa Clara, Cuba	66.4	77.8	85.3
25,131	Santa Clara, Cuba	66.0	79.1	83.4
52,000	Magdalena Mine, Cuba	47.8	58.2	82.1
21,415	Magdalena Mine, Cuba	51.6	58.1	81.9
47,615	Santa Clara, Cuba	58.4	77.4	75.4
	Impson Valley, Okla	48.9	91.8	53.2
	High	.	..	99.7
	Low	..	..	53.2
	Asphalt, Bermudez	94.9	95.6	99.2
	Gilsonite	99.7	99.8	99.9

On the ground of their relative solubility in turpentine the Impson Valley bitumen is differentiated from the West Virginia and the Cuban grahamites and all of them are more or less variable in this respect. This peculiarity should be further studied, including the bitumens from Colorado and Trinidad. In the case of the asphalts, it will be noticed, the bitumen is equally soluble in turpentine and in carbon disulphide, the lack of solubility in some of the grahamites undoubtedly being produced by changes due to environment and age.

It has been shown by the writer[1] that bitumens can be differentiated by the degree to which they are soluble in carbon tetrachloride, those showing the least solubility being the most metamorphosed by overheating, as in the preparation of residual pitches from asphaltic oils by distillation, or by age. The grahamites show decided differences in this direction. The proportion of bitumen in the several deposits examined varies, showing different degrees of alteration. The Colorado grahamite contains the largest amount of bitumen of this kind, over 80 per cent., the Oklahoma 58 and the Trinidad 39 per cent., while the Cuban deposits, with the exception of that at Bahia Honda, have but small amounts. This class of the components of bitumen has been called "carbenes" by the writer. A further study of this characteristic of the grahamites would prove of interest.

An interesting fact in connection with the mineral matter which is found in grahamite, and to which attention has been called by Messrs. Foster Hewitt and W. F. Hillebrand, is that, like the same component of some other bitumens, it contains vanadium, especially the ash of that from the Impson Valley, which contains from 11 to 15 per cent. of V_2O_5. The West Virginia grahamite contains 3.38 per cent., while Trinidad asphalt has 0.089, manjak a small amount and albertite a trace, according to determinations furnished by Dr. Hillebrand.

---

[1] *J. Soc. Chem. Ind.*, 24, 310 (1905).

From the facts and data given in the preceding pages grahamite can be characterized as a class of bitumens and further differentiated into sub-classes.

Grahamite may be defined as a brittle, solid native bitumen, the result of the metamorphosis of petroleum, generally pure but at times associated with adventitious mineral matter, characterized, when pure, by a peculiar schistose fracture, which has been termed hackly. It does not melt, but merely intumesces, on the application of heat, is soluble in carbon disulphide and only to a small extent in light naphtha and yields a high percentage of residual coke on ignition out of contact with air.

Various deposits of grahamite vary sufficiently to make it possible to divide them into several sub-classes:

1. Pure bitumens, 90 per cent. or more soluble in carbon disulphide.
2. Bitumens associated with adventitious mineral matter.

They may be subdivided again on a basis of solubility in naphtha, that is to say, the amount of malthenes which they contain, into:

3. Bitumens but a small proportion of which is soluble in light naphtha.
4. Bitumens of which a considerable part is soluble in naphtha, more than 15 per cent.

And still further, as regards the percentage of sulphur derivatives of the hydrocarbon which are present:

5. Bitumens with less than 5 per cent. of sulphur.
6. Bitumens with more than 5 per cent. of sulphur.

Individual grahamites can belong to more than one of these classes, but to only one in any group.

It is evident that the form of bitumen which we have had under examination is sharply differentiated from coal, asphalt and albertite and that there is no reason for confusing these minerals, as was done by the early writers. Whether there is any justification for further differentiating the grahamites and assigning names to special deposits, such as impsonite for the grahamite from Oklahoma, is a matter of opinion. From the writer's point of view this is, at present, hardly necessary. Particular grahamites have individual characteristics, but as a whole they are sufficiently alike to justify the application of the name to one class of bitumens, those which have been described in this paper, of which the original grahamite from West Virginia may be regarded as the type.

Eldridge, in his "Asphalt and Bituminous Rock Deposits of the United

States,"[1] classifies the solid native bitumens, excluding the melaterite and wurtzelite for some remarkable reason and giving no place whatever to asphalt, as asphaltite and coal, the former including albertite, impsonite, grahamite, nigrite and uintaite (gilsonite). Hofer has recently proposed to the writer that the solid native bitumens which are not asphalt shall be so denominated. It seems, however, that all these materials are so entirely different in character that we are hardly justified in putting them in one class, except for the fact that they are not asphalt, and the proposition does not, at present, commend itself.

In conclusion, the writer must acknowledge his indebtedness to the several assistants who have engaged in the investigation of the various grahamites and especially Mr. Kenneth Gerard Mackenzie, and Mr. J. S. Miller, Jr., for the study of the action of turpentine and tetrachloride of carbon on this bitumen. Prof. Jamieson and Mr. Ralph Langhy, of New Haven, have contributed ultimate analyses of several of the specimens, and have determined the presence of nitrogen, by the absolute method, in the Trinidad grahamite, Mr. Mackenzie has also aided in assembling the data and examining the cross references.

30 CHURCH ST., NEW YORK CITY

PROGRESS IN SYSTEMATIC QUALITATIVE ORGANIC ANALYSIS.[2]

BY S. P. MULLIKEN.

Received June 29, 1910

A general procedure in organic qualitative analysis that may be trusted to lead to the discovery of the proximate composition of any unknown organic substance whatever, whether this be a simple compound or a mixture, is demonstrably incapable of practical realization. Before proceeding to the discussion of the main subject of this paper, it therefore behooves us to pause for a moment to note certain limits which Nature seems to have set against the too curious advances of the analyst.

The most clearly insuperable of these limitations are associated with high molecular weight. If a paraffin hydrocarbon of the formula $C_{35}H_{72}$ were to be isolated in a state of perfect purity and in large quantity from some natural product, it would be impossible to absolutely identify it as a compound corresponding to any particular structural formula by any combination of methods of investigation now known, or whose future discovery appears probable. Such a hydrocarbon would not differ by one one-hundredth of one per cent. in its hydrogen or its carbon content from its adjoining homologues, while in chemical and physical properties there would be no measurable differences between it and thousands of its four million undiscovered structural isomers, which, according to the calculations of Cayley, are theoretically possible. Indeed, in the case of the discovery of such a high hydrocarbon by any process other than one of simple synthesis, no proof could be contrived which would show that the substance might not well be a mixture of many isomers and neighboring homologues; for all finite methods of purification by fractional separation based on differences in properties must inevitably fail when the numerical odds against them are so great, and we have no choice in such a case but to resign ourselves with the best grace possible to an inevitably partial solution of our problem.

---

[1] 22nd Annual Report U. S. Geological Survey, Part I, 209–452.

[2] An address delivered at the Second Decennial Celebration of Clark University, Worcester, Mass., Sept. 16, 1909.

But without having ascended to such an altitude in the homologous scale as in the instance just cited, it is often necessary or expedient to accept incomplete answers in qualitative inquiries because of our thralldom to the rule that unknown compounds in mixtures cannot in general be fully identified without previous isolation in a state of purity. It is for this reason that it is so common a practice in technical analysis to express the quantitative composition of familiar and important products in conventional or collective terms. Long and thoroughly as the animal fats have been studied, for example, there is probably no instance on record of a quantitative examination of any natural fat in which it could be safely claimed that the structural identity of all its fatty acids containing less than eighteen carbon atoms had been irrefutably established. Nor would it be surprising under the circumstances if such a result were never accomplished.

Thus handicapped, systematic qualitative organic analysis has developed slowly when compared with the simpler qualitative analysis of the inorganic elements and salts. Yet, if we contrast the difficulties to be overcome in constructing an orderly scheme for the separation and identification of the list of less than one hundred elements with the difficulties to be met in any corresponding scheme for the organic compounds, and then recall what has already been accomplished in overcoming them, and also the imperfections which present-day inorganic qualitative schemes still exhibit when the rarer elements are included, the organic chemist will find little cause for pessimism. The greater part of the contributions to organic qualitative analysis have been made, however, without much thought of the part which they might be made to play in any comprehensive scheme of procedure, and have often owed their origin to incidental observations made during the execution of investigations of broader scope and different purpose. Fischer's numerous characterizations of compounds in the sugar, purine and protein groups, by well chosen reactions and derivatives, and his ingenious separations for the amino acids formed in proteolysis are illustrations of this fact. Among the rather numerous handbooks of organic analysis, although many devote much space to qualitative testing, the speaker recalls only one whose author (Barfoed, 1878) has been sufficiently venturesome to incorporate the phrase "Organic Qualitative Analysis" in its title. Of the many commendable partial schemes for the isolation and identification, or the detection in certain classes of mixtures, of carbon compounds belonging to restricted groups, we owe the origin of a large proportion to an acute need of special analytical assistance in some department of industry, research, or governmental control. To such cause we owe much of what is most valuable in "Allen's Commercial Organic Analysis," Posts's "Chemisch-technische Analyse," and the works of Vortmann, Dragendorff, Hoppe-Seyler, König, Leach, Sherman, and others. The investigation of methods for the detection and determination of constituent radicals has also proved a fruitful source of valuable material, much of which has been made accessible for ready reference in H. Meyer's "Analyse und Konstitutionermittelung organischer Verbindungen."

The resolution of mixtures is usually the first, and often the most difficult part of a qualitative analysis. Definite plans for correlation in a broad general procedure of the methods of separation that have proved effective in the study of restricted classes of mixtures have yet to be proposed. The speaker is not in accord with the rather prevalent view that it is useless to strive for broader and more systematic separation procedures. But, on the other hand, as he is unprepared to play the prophet's rôle, it may be more profitable for him to confine the following discussion to the topic of systematic procedures for the identification of pure compounds, this being an important division of the qualitative problem whose solution seems nearer accomplishment.

Prior to 1831, the date of the inauguration of those revolutionary improvements in organic combustion methods by Liebig, which rendered it possible to determine the percentage composition of any carbon compound with considerable accuracy and comparative convenience, it does not appear that any comprehensive systematic methods for identifying previously described organic compounds had been formulated, or that the lack of them had been felt as a serious inconvenience. The number of pure compounds that had been described was comparatively small, the possibility of laboratory syntheses for organic compounds having only just become recognized, and the descriptions of such compounds as were known were not scattered as to-day through an almost endless list of special journals and treatises. A chemist of this earlier period, if a man of extended practical experience, well read, and having access to a good library, rested more or less content in the knowledge that he could probably accomplish by a purely eclectic procedure based on his miscellaneous sources of information, ingenuity, and common sense, all that was then analytically possible.

Thanks to Liebig's writings and the influence of the students who passed from his Giessen laboratory, his simplified methods of ultimate analysis were not long in becoming widely known. In scientific laboratories they were everywhere welcomed and adopted. This welcome was richly deserved; for, besides serving as a means to determine percentage composition values—which will perhaps always remain the most fundamental of chemical constants—their use, in connection with the later widely adopted vapor density molecular weight determination methods, furnished all information required for the calculation of empirical formulas. These, if we add knowledge of genetic relations and chemical behavior, become structural formulas with all the added information as to chemical characteristics and individuality which are inherent in the latter. The vapor density molecular weight determination methods reached their climax for the organic chemist in the air displacement form proposed by Victor Meyer in 1878. The prestige of the empirical formula as an aid in compound identification was soon still further enhanced by the discovery of Raoult's principle, followed by the invention of the Beckmann thermometer in 1888, these aids to molecular weight determination finally enabling the inclusion among the compounds of directly determined empirical formulas of a large share of the non-volatile compounds. Other causes about to be mentioned also conspired to bring the analytical importance of the empirical formula to extreme prominence.

During the two decades closing in 1880, the unprecedented increase in newly described organic compounds had already begun to assume the dimensions of a threatening deluge. The synthesist responsible for the creation of a new species, being aware of its genetic relations, and having determined its empirical formula, was usually in a position to correctly interpret the chemical identity of his progeny; though to prove that his discovery was really an original one by a search through the swollen literature had become a task to be undertaken with fear and trembling. The time rapidly approached when the healthy future development of organic research seemed likely to receive a serious check from the confusion and discouragement in store for investigators who could only hope to escape plagiarism in recounting their alleged discoveries by well-nigh interminable bibliographical delvings. Those of us in the younger generation of organic chemists are not in a position to even faintly appreciate the sigh of relief that must have been breathed by hundreds of workers in many lands when these chaotic conditions were ameliorated in 1882 by the completion of the first edition of Friedrick Beilstein's great handbook of organic chemistry. With rare foresight Beilstein had in season anticipated the mission which this remarkable work had to fulfil, and its publication after twenty years of incessant labor, occurring as it did at this critical period in the development of organic chemistry, is of epoch-making importance to organic qualitative analysis as well as to all other departments of the science.

Beilstein's "Handbuch" was a digest of the complete literature of the modes of formations, properties and reactions of all the analyzed compounds of carbon. It did not purport to be an analytical guide, and in its introduction the possibility of a qualitative organic analysis at all comparable to the inorganic is categorically denied. Nevertheless, because of the completeness and orderly arrangement of its concise descriptions, its importance as an aid in the identification of organic compounds may be fairly estimated as greater than that of all the special analytical treatises which have ever been issued. Its general classification for the compounds has some times been criticized as clumsy and confusing, but the division of species according to chemical function, saturation, and in homologous series, has, on the whole, served the interests of the analyst well; and the invention of a simple device for locating in its pages the description of any desired compound of known empirical formula, which has been more recently made available through the ingenuity and coöperation of M. M. Richter, the manager of the Prinz Dye Works in Carlsruhe, has now long served in case of compounds of this class to greatly facilitate their identification.

Richter's "Tabellen der Kohlenstoff-Verbindungen" with its 20,000 brief references to the literature and properties of the analyzed organic compounds was issued in 1884. The first volume of the second edition appeared in 1900 under the altered title of "Lexikon der Kohlenstoff-Verbindungen." In its present completed form this edition registers more than one hundred thousand compounds of determined empirical formulas, and gives direct access to the full description and literature of each by citation of the proper volume and page number of Beilstein. As a bibliographical index for compounds of known empirical formula it is hard to imagine anything simpler or more complete than the Richterian classification. The exact position of every possible compound (if we exclude the arrangement of isomers with reference to one another) is automatically fixed by its formula alone, and is as easily found, and in much the same manner, as a word in a dictionary through a knowledge of the relative positions of its letters in the alphabet. The completeness of the tabulation is suggestively indicated by the author's remark that his guiding thought during its preparation was "Das Unwesentliche, d. h. die weniger bekannten Verbindungen, stets in erster Linie und vollstandig hervorzuheben." On the other hand, its use as the basis for a method of identification for unknown organic compounds is often attended with serious or prohibitive difficulties.

It has been already pointed out that an absolute determination of species among the carbon compounds is theoretically impossible by any combination of tests in the case of compounds of extremely high molecular weight, and that the unavoidable errors of ultimate organic analysis with such substances are large enough to prevent analysts from making any selection between a large number of seemingly possible and equally probable empirical formulas. This unfortunate circumstance prohibits the use of the Richterian system in large and important fields where quantitative investigation by other methods may be conducted with good prospect of success. For example, the dyestuff tables of Schultz and Julius describe a hundred distinct tetra-azo dyestuffs having molecular weights above 500, and some of them exceeding 1000. These colors are many of them important, their constitutions well established by synthesis, and their identification through their physical and chemical properties, or at least their approximate identification--which is often all that is required—is not especially troublesome. The absurdity of an attempt to identify an unknown color of this class through its empirical formula—which would usually involve the quantitative determination of at least six elements with an impossible degree of precision—is so patent from the mere mention of the stoichiometric conditions that it may be hoped it has never been made by any rational being.

A second defect in the method of the empirical formula, which in the ordinary laboratory curtails its actual application even more than the absolute limitation just mentioned, is the fact that much special manipulation, skill and apparatus are necessary to ensure trustworthy results in elementary organic analysis, and that so much time is always consumed in the preliminary arrangements for a combustion and in its conduct. In the larger organic laboratories where the combustion of new synthetic products is an almost daily incident of the routine of investigation, and the equipment of the combustion room is maintained at all times in a state of perfect preparedness for emergency calls, so that no time need ever be lost in the mobilization for an analysis, the organic combustion is not formidable to the initiated. But under other circumstances—and they are the prevalent ones—chemists do not resort to the method of the empirical formula except under rather strong compulsion, and many identifications which ought to be made are not even attempted.

In view of these defects and inconveniences, it is natural to inquire whether there is hope of securing in the future any scientific substitute for the method of the empirical formula. In the comprehensiveness and simplicity of its classification of compounds, it must be admitted that it will be vain to expect anything but loss from radical changes in the Richterian arrangement; but, if we accept the logician's definition of a scientific classification as "Nothing more than a system of division carried out in such a way as to best serve a given purpose," and if our purpose is convenience and effectiveness in general qualitative investigation, the possibility of other and more scientific classifications is not to be denied; and it has seemed to the speaker that the discovery of such methods of classification is at present one of the important and attractive fields for organic chemical research. What the final outcome of this quest will be—if we have the right to speak of a final outcome in a problem which from its nature permits of only progressive partial solution—no one can as yet speak with full authority. Some of the general considerations bearing on the subject may, however, be brought to your attention.

Scientific classifications are chiefly concerned with relations of resemblance and contrast. To answer the question what points of resemblance and contrast must be regarded, and in what order, if we are to make a classification scientific, is to say that no basis of classification ("*fundamentum divisionsis*") is *per se* better than any other. All depends on the ultimate object. If the object of a classification is ready diagnosis of natural objects, it is evident that the characteristics used as *differentiae* for distinguishing between groups should permit of easy as well as certain determination; and it is also a good quality in such a division to collect individuals in the lowest group for comparison which are on the whole most alike. Methods of subdivision which aim at discovering something without regard to whether the resemblances of adjacent species are fundamental or accidental, like the classification of words in a dictionary according to the accidental alphabetical sequence of their letters, are called artificial systems. The Linnæan and Richterean systems belong to this category. No comprehensive system of division in natural science is free from many artificial features. But these are more likely to be prominent in the early than in the later stages of the development of a classification; the pioneer in such work having to first bridge his rivers with such structural materials as lie nearest at hand.

To the observant mind the discovery of possible *differentiae* for the classification of natural objects is an easy and fascinating pastime, though to make a wise selection may often be quite the reverse. Thus we read in the quaint diary of the botanist Linnaeus under the date of June 12, 1632, in his "*Lapland Observations*": "Close to the road hung the under jaw of a horse, having six front teeth, much worn and blunted, two canines, and at a distance from the latter twelve grinders, six on each side. If I knew how many teeth and what peculiar form, as well as how many udders, and where situated, each animal has, I should perhaps be able to contrive a most natural methodical arrangement of quadrupeds." As with Linnaeus' quadrupeds, so with organic compounds—we find a multitude of easily determined properties from which we may choose the *differentiae* for our classification, and by the exact coincidence of a sufficient number of these characteristics of different orders with those of an unknown compound, the identity of the latter may be proved. Qualitative elementary composition, color, melting and boiling point, specific gravity, odor, taste, solubility, refractive index, specific optical rotation, electrical conductivity, absorption spectra, color reactions, precipitations, and general chemical behavior—especially simple chemical reactions that throw light on the nature of dominant atomic groups and structural peculiarities—may all be thus used.

Regarding the chemical compound, or individual, as the *species* of a chemical system, it appears most natural to group these species in such a way as to make the next higher unit or *genus* contain species which are most similar in general chemical behavior. This would, for example, tend to make congeners of members of all homologous series containing the aldehyde radical, provided we could find sufficiently reliable and simple chemical tests for showing the presence of the CHO group. Recent chemical literature abounds in suggestions for tests suitable for generic *differentiae*, though much additional work will be required in every instance to determine the real value and exact boundaries of the genera that their employment would create, there being ever-present danger that overconfidence in the constancy of behavior of a reagent towards a given radical in different structural environments may lead to false conclusions. Thus, it is not safe to assume that under certain specified conditions all ketones will form oximes; all acids and phenols will dissolve in alkali; all esters will be saponified; or all unsaturated compounds will add bromine. In first delimiting a genus such assumptions may be adopted, after preliminary experiments, as tentative working hypotheses; but the contents and existence of the genus must be held to be strictly provisional and dependent on the positive outcome of the proposed genetic reaction when applied to a larger number of its carefully selected species, and to its negative outcome when tried with numerous members of all genera of higher numerical designation in the same classificatory *order*. It will also be the duty of the classifier to indicate, in a manner that will leave no doubt in the minds of readers, all descriptions, or parts of descriptions, for which he is personally responsible; for unless some means is given for distinguishing between data which he has verified, and others which he has not, the authority is liable to be more or less implicated in the mistakes of others for which he need have assumed no responsibility, but which will now tend to vitiate the value of his classification as a whole.

It would be premature at this time to present in all its minutiae any plan for such a classification as has just been suggested in its outlines. Details in illustration of the speaker's original conception and partial execution of such a plan are to be found in the already published first and third volumes of his "*Method for the Identification of Pure Organic Compounds.*" All that is desired here is to lead to a discussion of the advantages in the plan for Chemistry; and, if it is sound, to arouse interest with a view to eventually bringing about a wider coöperation for furthering its future development. The difficulties to be overcome are considerable. Recorded descriptions of organic compounds, while frequently very complete for a few properties like melting and boiling points, are commonly equally deficient concerning others—especially in exact data showing the extent of the influence of slight variations in chemical constitution on the results of the selected differential tests. The occasion hence arises for an investigation or partial reexamination of a considerable proportion of the species receiving locations. If one has the pure compounds with which to experiment, the tests are easily made. But as only a few thousand pure compounds can be procured through commercial channels, and most of these require some purification, success in the construction of a comprehensive diagnostic classification implies assistance from private collections throughout the world; for to synthesize any considerable part of the rarer species would overtax the facilities of the largest and best equipped of laboratories.

To bring a majority of the carbon compounds referred to in Richter's Lexikon into an essentially "natural" classification of the kind suggested would, assuming the study of tests and revision of constants to be thoroughly done, perhaps involve a labor as great as the transformation of the "artificial" botanical classification of Linnaeus into the modern "natural" system as it was left by de Candolle. An undertaking of this magnitude and character might presumably in the present century be accomplished with greater benefit to science under the direction of some such organization as the committee entrusted with the periodical revision of Beilstein's "Handbuch" and the Richter "Lexikon" than under private auspices.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.

[CONTRIBUTION FOR THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

SYNTHESIS OF THE α,α'-DIMETHYLADIPIC ACIDS, AND SEPARATION OF THE RACEMIC ACID INTO OPTICAL ISOMERS.

BY WILLIAM A. NOYES AND L. P. KYRIAKIDES.

Received June 24, 1910.

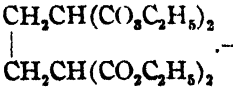
The α-α'-dialkyl-dicarboxylic acids are described in the literature as existing in two stereomeric forms—known as maleinoid and fumaroid. As far as we know none of these acids have been resolved into optical isomers. Bischoff and Walden[1] have failed in the resolution of the succinic acids. And because of this failure, the view has been entertained, that in such cases even saturated molecules are fixed in space, so that the singly-bound group or atom can not rotate.[1]

---

[1] *Ber.*, 22, 1814.

By glancing at the structure of α,α′-dimethyladipic acid, we see that this acid, like tartaric acid, has two asymmetric carbon atoms, and consequently, according to van't Hoff's theory, it ought to be resoluble into optical isomers. As will be seen later, we have succeeded in effecting this resolution.

Ethyl Ester of Butanetetracarboxylic Acid,



$$\begin{array}{l} CH_2CH(CO_2C_2H_5)_2 \\ | \\ CH_2CH(CO_2C_2H_5)_2 \end{array}$$

.—At first we prepared this compound in toluene. The best yield was obtained by using an excess of sodium, about one and one-half times that required theoretically in the malonic ester condensation. The sodium was shaken to granules in boiling toluene. The mixture was cooled, and equivalent portions of ethylene bromide and malonic ester were added. After three hours' cooling, the mixture was heated on the steam bath for about 15 hours. In this way from the pure malonic ester as well as from the recovered malonic ester, about 27–30 per cent. of the theoretical yield of butanetetracarboxylate boiling between 230–250° at 40 mm. was obtained.

Meunier[2] has described the use of magnesium in the form of amalgam instead of sodium in the preparation of mono- and diethylmalonic ester. We have tried this method in the preparation of butanetetracarboxylate, and find it better, in this case, than the use of sodium.

Ten grams of clean magnesium ribbon were put in a 500 cc. round-bottomed Jena flask, 400 grams of mercury added, and the mixture heated and shaken until the amalgamation was complete. The flask was then provided with a protected reflux condenser, 100 cc. of absolute alcohol was added, and the mixture heated on the steam bath for three hours. Occasional shaking of the flask, vigorously, hastens the formation of the magnesium ethylate by breaking the crust that clings to the sides of the flask. The flask was then cooled somewhat, and 100 grams of malonic ester were added, care being taken that the liquid did not boil too vigorously. When the reaction subsided, the flask was heated on the steam bath for three hours more. The alcoholic solution of the magnesium malonate was then cooled somewhat, 58 grams of ethylene bromide added, and after a short time the mixture was heated on the steam bath for 10–14 hours.

The alcohol was distilled off as much as possible under reduced pressure and the reaction mixture was treated with water and hydrochloric acid

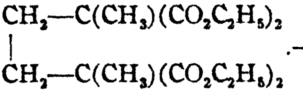
[1] Lean, *J. Chem. Soc.*, 65, 1001.

[2] *Compt. rend.*, 137, 714.

until the liquid separated into two layers. Ether was then added, the mixture shaken, and the ethereal solution separated and washed twice with dilute hydrochloric acid in order to wash away any magnesium held by the butanetetracarboxylate. After drying with sodium sulphate the ether was evaporated off, and the residue fractionated under reduced pressure. In this way 40–43 grams of the butanetetracarboxylate were obtained, boiling between 210–230° at about 10 mm. A low pressure is essential for successful fractionation of the product.

From each condensation about 40 grams of malonic ester were recovered, and used in subsequent condensations. The yield is, therefore, from 65 to 70 per cent. of the weight of malonic ester used or from 60 to 65 per cent. of the theoretical. The method is much less troublesome and, so far as we can judge from his statements, gives better yields than the method of Perkin.[1]

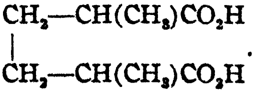
Ethyl Ester of Dimethylbutanetetracarboxylic Acid,



$$\begin{array}{l} CH_2—C(CH_3)(CO_2C_2H_5)_2 \\ | \\ CH_2—C(CH_3)(CO_2C_2H_5)_2 \end{array}$$

.—Ten grams of sodium were dissolved in about 120 cc. of absolute alcohol, the solution was cooled in ice water, and a mixture of 70 grams butanetetracarboxylate and 64 grams of methyliodide was added drop by drop, while the flask was continually shaken to keep the mixture from getting warm. It was found that the yield in the product was much greater when the mixture was kept thoroughly cooled. After the mixture had stood in the cold about half an hour it was warmed on the steam for an hour or two, while the flask was connected with an upright condenser. The alcohol was then evaporated off under reduced pressure. Water and a little hydrochloric acid were added. The ester was taken up in ether, washed with dilute potassium hydroxide, dried, the ether evaporated off, and the ester left to crystallize. The ester was purified by recrystallization from petroleum ether.[2] The yield of the recrystallized product was about 85 per cent. By working with smaller amounts we have succeeded in obtaining as high as 95 per cent. of the theoretical.

α-α'-Dimethyladipic Acids,



$$\begin{array}{l} CH_2—CH(CH_3)CO_2H \\ | \\ CH_2—CH(CH_3)CO_2H \end{array}$$

.—These were prepared from the pure crystallized dimethyl butanetetracarboxylate by the method of Lean[3] by boiling for 16 hours with a mixture of 350 cc. each of water and concentrated sulphuric acid. 165 grams of the dimethyl butanetetracarboxylate gave the theoretical amount of the adipic acids. The separation of the mixture into the two modifications, known as the fumaroid, and maleinoid, was carried out by a combination of the methods of Zelinsky[1] and Lean,[2] that is, by crystallizing from water and benzene. The final crystallizations were from water.

---

[1] *J. Chem. Soc.*, 65, 578.

[2] Lean, *J. Chem. Soc.*, 65, 1004.

[3] *Loc. cit.*

The dried acids melted at 143 and 70°. The lower melting modification begins to soften at 65°. Zelinsky gives the melting points as 140–141° and 74–76°. Lean gives 142° and 70–72°.

Separation of the Racemic α,α'-Dimethyladipic Acid into its Optical Isomers.—Twenty-seven grams of the acid melting at 70° were dissolved in 450 cc. of water, and 32 grams of brucine were gradually added to the hot solution. 131 grams brucine are necessary to neutralize completely the 27 grams of the acid. We have used about one-fourth of the weight of brucine, theoretically required, with the object of forming the acid-salt of the less soluble optically active acid. The solution, while hot, was inoculated with a few crystals of the brucine salt from a former preparation, and the liquid left overnight. The crystals were collected on a filter, and washed four times with about 15 cc. of water each. They were then dissolved in 250 cc. of hot water and crystallized. One more crystallization from 150 cc. of water is all that is necessary.

The salt was dissolved in about 150 cc. water, decomposed with sodium hydroxide, cooled in ice, the solution of the sodium salt of the acid filtered off from the alkaloid, and the latter washed several times with cold water.

The aqueous solution was treated with hydrochloric acid, a little in excess of the amount required to neutralize the sodium hydroxide used. The acid was then extracted 5 times with ether, the latter evaporated off, and the acid crystallized once from a little water. The acid thus obtained gives a positive rotation of $(\alpha)_D^{28°} = +31.3°$ in 10 per cent. alcoholic solution. It begins to soften at 103.5° and melts completely at 105.5°. Yield, 7 grams A sample of the acid (0.1741 gram) titrated required 20.02 cc. 0.1 *N* potassium hydroxide. Theory, 20.00 cc. For the *l*-acid the mother liquor from the first crop of the brucine salt, in the preparation of the *d*-acid, was extracted with ether. The acid thus obtained melted at 70–95°.

Ten grams of this acid were dissolved in 150 cc. water and 11 grams of brucine added. The crystals that separated were recrystallized from diminishing amounts of water four times. The acid that was liberated and purified as in the case of the dextro acid, melted at 85–103° and gave a rotation of $(\alpha)_D^{28°} = -23.4$ in 10 per cent. alcoholic solution. A sample titrated required 4.02 cc. 0.5 *N* potassium hydroxide. Theory, 4.00 cc. The rotation in comparison with that of the dextro acid indicates that this acid still retained about 12 per cent. of the dextro form.

---

[1] *Ber.*, 24, 3997.

[2] *J. Chem. Soc.*, 65, 1006.

Lack of time and material prevented us from carrying the purification of the levo form further.

An attempt to separate the fumaroid form of the α-α′-dimethyladipic acid (m. 143°) into optical isomers by means of its brucine salt was unsuccessful. It is undoubtedly a "meso" form, optically inactive by internal compensation.

Summary.

By using magnesium amalgam for the preparation of magnesium ethylate and condensing ethylene bromide with malonic ester by means of the latter the yield of butanetetracarboxylic ester has been greatly improved and this compound is now rather easily accessible.

The *dl*,α,α′-dimethyladipic acid (m. 70°) has been resolved into its optical components, of which the dextro form has been obtained in a state of purity. It melts at 104–105° and has a rotation $(\alpha)_D^{28°} = +31.3°$ in a 10 per cent. alcoholic solution.

The levo form was only obtained in a relatively impure form, melting over a wide range and given a rotation $(\alpha)_D = -23.4°$.

The "meso" form of α,α′-dimethyladipic acid (m. 143°) gave no indication that it could be separated into optically active components by crystallization with brucine.

The separation of the racemic α-α′-dimethyladipic acid into its optically active components definitely disproves the view expressed by Lean[1] that the carbon atoms are so united in this and similar cases that optical isomerism is impossible. These acids exist in four forms in close analogy with the four tartaric acids and in strict accord with the theory. The synthesis of laurolene from α-α′-dimethyladipic acid will be described in a subsequent paper.

URBANA, ILLINOIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. III. OXIDATION PRODUCTS OF *l*- AND *d*-LAUROLENE.[2]

BY WILLIAM A. NOYES AND C. G. DERICK.

Received June 24, 1910.

Levo-laurolene.

In a previous paper[3] it was shown that laurolene, when prepared from the nitroso derivative of aminolauronic anhydride by boiling with sodium hydroxide solution, always gave an optically negative hydrocarbon,

---

[1] *Loc. cit.*

[2] Abstract of one part of a thesis presented by Mr. Derick to the Graduate School of the University of Illinois in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[3] Noyes and Derick, THIS JOURNAL, 31, 670.

C_8H_{14}. This work has been repeated and the hydrocarbon from different preparations gave $(\alpha)_D^{29°} = -15.72$ and $(\alpha)_D^{27°} = -18.13$. The value of the negative rotation changes with the method of preparation, as Crossley and Renouf[1] have previously shown. The higher value of the rotatory power was found when the hydrocarbon was distilled from its sodium hydroxide solution as rapidly as it was formed. It would seem that longer contact with the alkaline solution causes the racemization of a part of the laurolene.

This product upon oxidation gave the diketone mentioned in the first article. Contrary to the statement made at that time, the diketone does not easily condense. In fact it gives very constant boiling point determinations with no evidence of decomposition. The boiling point,[2] under 750 mm. pressure, is 204° (cor.). The optical activity was found to be $(\alpha)_D^{36.5°} = 0.53°$ while that of the previous preparation[3] was found to be $(\alpha)_D^{25°} = -8.47°$. Hence it is evident that the diketone, like the hydrocarbon, possesses an optical rotation which varies with the method of preparation.

The diketone forms an oily dioxime, which gave upon analysis:

Calculated for $C_8H_{16}N_2O_2$: N, 16.27; found: N, 15.45.

An oily monophenylhydrazone was obtained which gave upon analysis:

Calculated for $C_{14}H_{20}ON_2$: N, 12.07; found: N, 12.72.

Although these analyses were made with products which could not be carefully purified they are sufficiently accurate to show that the oxidation product of *l*-laurolene is a diketone.

In the case of the semicarbazone, more satisfactory results were obtained in the form of a white crystalline product melting at 194° (cor.) The substance separates very slowly from the solution in which it is prepared. It was not found possible to recrystallize it. The portion used for the melting point and analysis was washed thoroughly with warm water (about 60°) till free from chlorides. The analysis gave:

Calculated for $C_{10}H_{20}O_2N_6$:	C. 46.87	H, 7.82	N, 32.81
Found:	46.50	8.80	31.71

These analyses were made with very small amounts, since the yield of the disemicarbazone was very small and much time is required for the preparation. But the results prove beyond a doubt that the oxidation product of laurolene is a diketone.

Attempts to condense the diketone by heating alone and with sodium hydroxide were unsuccessful. Phosphorus pentoxide gave a very small yield of a product, boiling at 143°, which could not be further investigated.

---

[1] Crossley and Renouf, *J. Chem. Soc.*, 89, 38.

[2] This was determined by Sivolobov's method, *Ber.*, 19, 795, as modified by Mulliken, "A Method for the Identification of Pure Organic Compounds," p. 222.

[3] Noyes and Derick, *Loc. cit.*

A diketone of the formula $C_8H_{14}O_2$ must necessarily be an open chain compound. This view of its structure receives strong confirmation from the synthesis of laurolene (see the following paper) and from the boiling point and specific gravity of isomeric diketones.

	Boiling point.	Specific gravity	
2,3-Octanedione $CH_3(CH_2)_4COCOCH_3$.	172–173°	732 mm.	. . . . .[1]
3,4 Dimethyl 2,5-hexanedione, $CH_3COCH(CH_3)CH(CH_3)COCH_3$	210°	. . . .	. . . . .[2]
3-Methyl-2,4 heptanedione, $C_3H_7COCH(CH_3)COCH_3$	89-90°	20 mm.	0.955[3]
3 Methyl-2,6-heptanedione, $CH_3COCH(CH_3)CH_2CH_2COCH_3$	203–204°	750 mm.	0.988[4]

In general the specific gravities and boiling points increase as the carbonyl groups are further apart.

The presence of the acetyl group in the diketone was also demonstrated by the formation of bromoform when it is treated with sodium hypobromite. The diketone reduces a neutral solution of potassium permanganate instantly, as acetone does.

Dextro-laurolene.

In our previous article on laurolene, we stated that the direct decomposition of the hydrochloride of aminolauronic acid by means of sodium nitrite always gave an optically positive hydrocarbon, C_8H_{14}. Similar results have been obtained since the publication of the above article. The rotation of laurolene prepared in this manner being $(\alpha)_D^{26.2°} = +28.15°$. The rotation of the hydrocarbon varies, therefore, with the method of preparation as was found to be the case with the optically negative laurolene. The density of the optically positive laurolene was found to be $d_{4°}^{15°} = 0.8030$ and $d_{20°}^{20°} = 0.7991$. The boiling point was 120.3–121° at 750 mm. Thus levo- and dextro-laurolene possess the same composition, boiling points and density.

Oxidation of dextro-laurolene by the same method employed with levo-laurolene gave a diketone. It was also purified by fractional distillation with a Sprengel pump and distilled from 70–80° under ½ to 1 mm. pressure. The product gave upon analysis:

Calculated for $C_8H_{14}O_2$: C, 67.60 ; H, 9.86 .
Found: C, 66.53, 66.50, 67.9; H, 9.90, 10.15, 10.60.

The analysis of the diketone was very difficult. If burned in an open boat the results were uniformly too low, while if burned in a bulb with copper oxide it was exceedingly hard to burn the last traces of carbon. Extra long burning with some copper oxide in the bulb with the diketone gave the last analysis, which is within the limits of experimental error for carbon. The results show that a diketone is formed which boils at the same temperature as the diketone from levo-laurolene.

---

[1] Ponzio and Prandi, *J. prakt. Chem.*, (2) **58**, 402.

[2] Demétre Vladesco, *Bull. soc. chim.*, (3) **6**, 809.

[3] Bouveault and Bongert, *Ibid.*, **27**, 1087.

[4] Noyes and Derick, THIS JOURNAL, **31**, 672.

Several determinations of the optical activity of the diketone from dextro-laurolene, as above prepared, showed it to be optically inactive. Experiments were performed with the diketone in the pure form as well as in 20.5 per cent. ethereal and alcoholic solutions.

As in the case with diketone from levo-laurolene, the diketone from dextro-laurolene gave an oily oxime and phenylhydrazone.

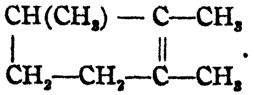
The semicarbazone was a white crystalline product which separated from water after long standing. It melted fairly sharply at 192° (cor.) and appeared to resolidify and again melt at 225° (cor.). A very recent preparation gave a semicarbazone which melted at 228° (cor.) with no evidence of a preliminary melting. The analysis of the product melting first at 192° gave:

Calculated for $C_{10}H_{20}O_2N_6$: N, 32.81. Found: N, 33.25

It is evident that the oxidation product of dextro-laurolene is a diketone identical with the diketone obtained from levo-laurolene. Therefore dextro- and levo-laurolene are mixtures of optical isomers, but the *d*- and *l*-forms occur in different proportions. In the levo-laurolene the *l*-form predominates while in the dextro-laurolene the *d*-form is in excess.

Structure of Laurolene.

The experiments described in this paper give further confirmation of the structure of laurolene first proposed by Eijkman[1] on the basis of refractometric studies and advocated by us in our previous paper.[2] They have shown, also, that both *d*- and *l*-laurolene give a diketone by oxidation and that the semicarbazones of the ketones from the two hydrocarbons are, apparently, identical, indicating that the two hydrocarbons differ only in configuration and are otherwise identical in structure. The formula established for laurolene is,



URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. IV. SYNTHESIS OF LAUROLENE.

BY WILLIAM A. NOYES AND L. P. KYRIAKIDES.

Received June 24, 1910.

Of the two hydrocarbons having the formula C_8H_{14}, the structure of isolaurolene has been established synthetically by Blanc.[3] Eijkman,[4] having studied the optical properties of laurolene, has proposed the structure

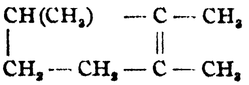
---

[1] *Chem. Weekblad*, 1906, No. 45; 1907, No. 4; *Chem. Zentr.*, 1907, II, 1208.

[2] THIS JOURNAL, 31, 671.

[3] *Bull. soc. chim.*, (3) 19, 703; *Compt. rend.*, 142, 1084.

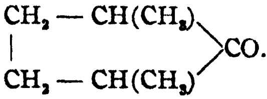
[4] *Chem. weekblad.*, 1906, No. 45; 1907, No. 4; *Chem. Zentralbl.*, 1907, II, 1208.



for this hydrocarbon.

Noyes and Derick[1] have given experimental evidence in favor of the formula proposed by Eijkman. They oxidized laurolene, and obtained an active diketone. The only formula for laurolene—an active body itself—consistent with this behavior on oxidation is that proposed by Eijkman.

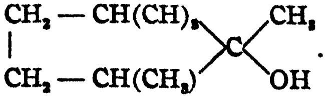
The object of the present investigation has been to establish the constitution of laurolene by synthesis. As will be seen, we have verified experimentally the constitution of laurolene, as given above.



Preparation of 2,5-dimethylcyclopentanone.—The separation of *dl*,α,α'-dimethyladipic acid into its optically active components[2] was undertaken in the hope that this might be the starting point for the preparation, synthetically, of an optically active laurolene. When the dextro-α,α'-dimethyladipic acid was mixed with lime and distilled, the resulting dimethylcyclopentanone proved to be optically inactive.

Having failed to secure an optically active ketone, in our further experiments the mixture of "meso" and racemic α,α'-dimethyladipic acids obtained by the saponification of dimethyl ketonetetracarboxylic ester (see preceding paper) was used. Portions of 12 to 13 grams of these acids were mixed with about 25 grams of calcium oxide and the mixture placed in a small distilling bulb, of such size that it was nearly filled. The bulb was placed in a bath of Wood's metal and heated until the ketone was formed and distilled away.

By this method 73 grams of the α,α'-dimethyladipic acids gave 33 grams of the purified ketone boiling at 146–149°, the main portion at 147–148°. This is about 70 per cent. of the theoretical yield. Zelinsky and Rudski[3] give the boiling point as 145–147°. Better yields of the cyclopentanone are obtained by distilling the acid in portions of 6 grams each.



1,2,5-Trimethylcyclopentanol-1. — This compound was prepared from the dimethylcyclopentanone by means of the Barbier-Grignard reaction. Eight grams of clean magnesium ribbon were put in a flask, with 25–30 cc. absolute ether and 50 grams of methyl iodide were added, the flask being provided with a protected reflux condenser. As soon as the reaction became vigorous, the reaction mixture was cooled. Towards the end, it was heated gently on the steam bath. When the solution of the magnesium was complete, the solution was cooled in ice water, and shaken continuously, while 30 grams of the cyclopentanone were added drop by drop, on account of the violence of the reaction. The mixture was left in the cold for about a quarter of an hour and then warmed on the steam bath for an hour. The reaction product soon separated out as a solid.

---

[1] This Journal, 31, 669.

[2] *Ibid.*, 32, 1057.

[3] *Ber.*, 29, 304.

The ether was then mostly evaporated off, and the product added slowly to crushed ice, while the latter was being stirred. Local heating is to be avoided, as the alcohol has a strong tendency to decompose.

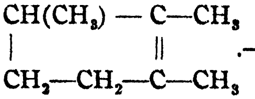
Ice-cold acetic acid was slowly added until the liquid separated into two clear layers. The upper layer was separated, washed once with dilute acetic acid, twice with dilute potassium hydroxide, and dried quickly over sodium sulphate. The cyclopentanol was then fractionated under a very low pressure.

The substance boils at 56–60° in the neighborhood of 8 mm. Yield about 65 per cent.

Analysis:	Calculated for $C_8H_{16}O$:	C, 74.98	H, 12.68
	Found:	C, 74.44	H, 12.74

The specific gravity was $d_{4°}^{15°} = 0.9121$.

The refractive index as read on the Abbé refractometer and corrected was $n = 1.4554$ at 16.7°.

Synthetic laurolene, C_8H_{14} or  $\begin{array}{l} CH(CH_3) - C-CH_3 \\ | \qquad\qquad\quad \| \\ CH_2-CH_2-C-CH_3 \end{array}$.—Simply heating the cyclopentanol at ordinary pressure induces the breaking off of a molecule of water. However, complete dehydration in this way is a tedious process. In order to obtain the pure unsaturated hydrocarbon, we have usually used Zelinsky's method.[1]

Eleven grams of the cyclic alcohol, which had lost most of its water by two distillations at ordinary pressures, were mixed with 10 grams of powdered anhydrous oxalic acid, heated at 100–110°, and distilled. Repeating the heating with oxalic once more, and subjecting the distillate to steam distillation, drying the product over calcium chloride, and fractionating, we obtained the hydrocarbon boiling at 119–122°. The specific gravity was $d_{4°}^{15°} = 0.8039$.

Analysis of the hydrocarbon after it had stood a month:

Calculated for C_8H_{14}:	C, 87.27 ;	H, 12.72
Found:	C, 87.06, 87.16;	H, 13.15, 13.03.

---

[1] *Ber.*, 34, 3249.

In the last preparation of the hydrocarbon we used phosphorus pentoxide as a dehydrating agent. It was necessary to dry the cyclopentanol over phosphorus pentoxide and distil several times before the dehydration was complete. The final fractional distillation gave a product that disti[illegible]mostly at 121.6°. The hydrocarbon prepared in this way was foun[illegible] oxidize rapidly in the air, so that the substance two weeks after its preparation gave 73.86 per cent. carbon instead of the theoretical 87.72 per cent.

In order to free the hydrocarbon from the oxidation product, the mixture was fractionated, and the fraction boiling up to 125° collected. This was then subjected to steam distillation, until the volume of the distillate was about 10 cc. This was dried, and fractionated, when about 5 grams of the hydrocarbon boiling at 120–122° was obtained.

Analysis of the product immediately after distillation:

Calculated C, 87.27, H, 12.72. Found: C, 86.90; H, 12.94

The refractive index of the hydrocarbon was = 1.4464 at 16.5°.

In the purification of the alcohol and hydrocarbon we observed the same characteristic green coloration which was observed by Walker and Henderson[1] and which we have often noticed in working with lauronolic acid and laurolene.

The hydrocarbon was oxidized with the theoretical amount of a 2 per cent. solution of potassium permanganate in the cold. The oxidation product was extracted several times with ether, directly from the oxidation mixture On fractionating the product, about 0.6 gram of substance was obtained boiling at about 75° in the neighborhood of 5 mm.

Analysis: Calculated for $C_8H_{14}O_2$. C, 67.60; H, 9.86
Found. C, 69.79, 70.09; H, 10.42, 10.36.

The substance that was obtained as oxidized in the air, was treated with a little 2 per cent. solution of potassium permanganate and purified. It was analyzed, and gave: C, 71.93; H, 10.59. Working with about 5 grams of the hydrocarbon and the yield in the oxidation product being so poor, we could not expect a very pure product. However, comparison of this oxidation product, with that obtained by Noyes and Derick[2] by the oxidation of the laurolene from the decomposition of aminolauronic acid, shows that they are the same. Noyes and Derick give as the boiling point of their diketone 203.6°. (See the preceding paper). Two samples of our oxidation product, prepared from two distinct preparations of the hydrocarbon, gave 203° and 204° as the boiling points of the oxidation products, respectively.

Noyes and Derick give 0.9844 as the specific gravity of their pure diketone. The one last prepared by us gave 0.9733 at 20°. Both the lower specific gravity and the analyses indicate that the diketone retained a small amount of the hydrocarbon from which it was impossible to separate it owing to the small amount available.

---

[1] *J. Chem. Soc.*, **49**, 749.

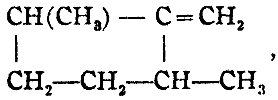
[2] THIS JOURNAL, **31**, 669.

Comparison of constants of the hydrocarbons:

	Boiling point.	Sp gr. at 15°.	n at 16.5°.
C_8H_{14} from aminolauronic acid	120–122°	0.8030	1.[illegible]
C_8H_{14} synthetic.......................	120–122°	0.8039	1.[illegible]64

The structure of laurolene as Δ′-1,2,3-trimethylcyclopentone must therefore be considered as fully established.

Professor Eijkman has kindly determined the refractometric constants of our synthetic laurolene. He finds the refractive index slightly less than that of the laurolene from camphor, as we have done. He also finds the dispersion somewhat less and suggests that the synthetic laurolene may contain some *pseudolaurolene*, , which would account for the difference. We hope to publish Professor Eijkman's results with laurolene and with some of the other compounds later.



URBANA, ILL., August, 1910.

[CONTRIBUTION FROM THE LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

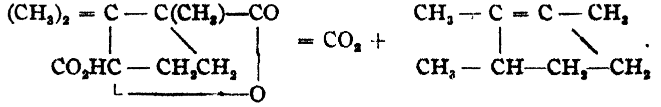
MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. V. MECHANISM OF THE REACTIONS BY WHICH LAUROLENE IS FORMED.

BY WILLIAM A. NOYES.

Received June 24, 1910.

Having established the structure of laurolene (see the preceding papers) it is now possible to discuss intelligently the reactions by which it is formed. The most important of these are the following:

1. By the slow distillation of camphanic acid[1] or by distilling calcium camphanate[2]



The yield is 53 per cent. of the theoretical (Aschan) and the hydrocarbon is sometimes levorotatory and at other times dextrorotatory.

2. By the distillation of lauronolic acid[3] (allocampholytic acid):

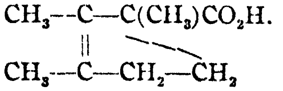
$$C_8H_{13}CO_2H = C_8H_{14} + CO_2.$$

---

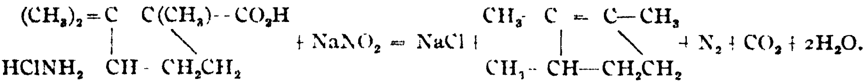
[1] Wreden, *Ann.*, 163, 336; Aschan, *Ann.*, 290, 187; Zelinsky, *Ann.*, 319, 311; Crossley and Renouf, *J. Chem. Soc.*, 89, 27.

[2] Rupe and Maull, *Ber.*, 26, 1202.

[3] Walker and Henderson, *J. Chem. Soc.*, 69, 749.

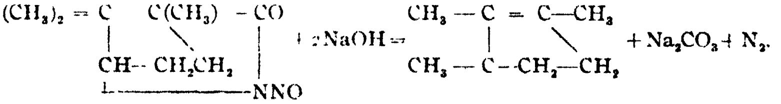
The yield is not given and there is some indication that the allocampholytic acid used was a mixture. The hydrocarbon obtained was levorotatory. The shifting of the methyl group in this case may have occurred either during the formation of the lauronolic acid or during its decomposition to form laurolene. On the basis of refractometric measurements Eijkman concludes that the former is the case[1] and that the structure of lauronolic acid is  It is our intention to study this question further from the chemical side.

3. By the interaction of sodium nitrite and the hydrochloride of aminolauronic acid.[2]

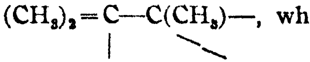


The yield is 19 per cent. of the theoretical[3] and the hydrocarbon is dextrorotatory.

4. By heating the nitroso derivative of aminolauronic anhydride with sodium hydroxide.[4]



The yield is 53 per cent. of the theory and the hydrocarbon is levorotatory.

A consideration of these reactions leads us to the conclusion that the decompositions which take place lead to the formation of the complex  which is, of course, incapable of an independent existence. Under these conditions one of the "gem" methyl groups shifts to the lower carbon atom giving an opportunity for the formation of a double union between the two upper carbon atoms of the ring. Erlenmeyer[5] suggested the intermediate formation of a trimethylene ring in such cases but the fact that phenyl groups may shift their places as easily as methyl and that atoms in the para position in such phenyl groups remain para,[6] has rendered this explanation almost untenable. It seems much simpler to assume that one of the methyl groups is momentarily detached only to combine at once with the adjacent carbon atom.

---

[1] Private communication.

[2] Noyes, *Am. Chem. J*, 17, 432.

[3] Noyes and Derick, This Journal, 31, 671.

[4] Noyes and Taveau, *Am. Chem. J.*, 35, 379. See also This Journal, 31, 671.

[5] *Ber.*, 14, 322.

[6] Montague, *Rec. trav. chim.*, 24, 105; 25, 413.

The loosening of the affinity of the "gem" methyl groups for the carbon atom to which they are attached through the free valences of the two carbon atoms to which that carbon atom is attached is probably an important factor in the reaction.[1] About the only apparent objection to the view here expressed is the ordinary experience with carbon compounds that carbon atoms do not readily separate from each other. But we know that at higher temperatures or in the presence of negative groups such separations do frequently occur. That the parts which separate may recombine to a more stable grouping is to be expected. For the pinacone-pinacolin rearrangement and also for the α- and β-campholytic acids it has been shown that the shifting of the methyl group may be reversible, which points strongly to the probability that separation between carbon atoms may be much more frequent than we have supposed. Only in those cases where an opportunity is presented for a more stable grouping will the separation result in a rearrangement. The fact that laurolene has a higher specific gravity and boiling point than isolaurolene makes it extremely probable that its heat of combustion is also higher and that the shifting of the methyl group is accompanied by a dissipation of energy. Isolaurolene, of course, more nearly retains the structure of camphor. It is, perhaps, worth while to call attention to the fact that in the decompositions of camphanic acid and of the nitroso compound, in both of which cases the two carbon atoms of the ring are associated by a cyclic grouping, the loss of carbon dioxide and formation of laurolene occurs in much larger amount than it does in case 3 where the primary decomposition affects the amino group only.

It may also be remarked that if we assume that these reactions are ionic in character the free valences in the intermediate product will be positive and negative respectively and that the methyl group which shifts its place would be negative as it does so. This is in accord with the hypothesis first proposed by the writer in 1901[2] that atoms of the same element may in different cases assume either positive or negative charges. Essentially the same fundamental idea has been proposed quite independently by Abegg[3] and, from a wholly different point of view, by J. J. Thompson.[4]

The loss of carbon dioxide in these reactions is probably closely related to the loss of carbon dioxide by any ion of an organic acid when it loses its negative charge at the anode in electrolysis.

URBANA. ILL.

---

[1] THIS JOURNAL, 31, 1373.

[2] *Ibid.*, 23, 463 (1901).

[3] *Z. anorg Chem.*, 39, 343 (1904).

[4] "The Corpuscular Theory of Matter," p. 130 (1907).

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE HYDROCARBONS OF THE WOOL GREASE OLEINS. FIRST PAPER.

BY AUGUSTUS H. GILL AND LAURENCE R. FORREST.

Received June 30, 1910

In 1904 Gill and Mason showed how these hydrocarbons might be distinguished from mineral oil.[1]

The hydrocarbons were obtained by saponifying the distilled wool grease oleins with an excess of alcoholic potash. The unsaponifiable matter was extracted with redistilled petroleum ether, treated with acetic anhydride to remove any cholesterol, and if more than 0.2 cc. of 0.5 *N* alcoholic potash per gram of oil were required for the saponification of the neutral oil present, these operations repeated until an oil of this quality resulted.

The oil obtained has the following characteristics (for comparison those of some mineral oils are herewith shown).

		Bromine			
	Sp gr at 15°.	Addition	Substitution	Optical rotation in 200 mm. tube.	Refractive index at 20°.
	0.896	28.8	14.2	+17° 58′	1.4967
Mineral oils	0.848-0.863	4.4-5.9	5.6-8.4	+ 1° 2′	1.4662-1.4750

From the large bromine addition number these hydrocarbons would seem to be unsaturated compounds, and according to the investigations of Smith[2] to have been formed by the breaking down of an ester, like cetyl palmitate, into the corresponding acid and the double-bonded hydrocarbon of a similar name, $C_{15}H_{31}COOC_{16}H_{33} = C_{15}H_{31}COOH + C_{16}H_{32}$. Between two and three liters of these hydrocarbons were prepared from the olein as above described. Some of this was distilled at a pressure of 17–44 mm. giving boiling points from 270° to 315°; good separations were not obtained, it being impracticable to use a bead tower, five or six inches of vertical height being as much as the liquid could be raised by boiling.

Fractionation under these circumstances being difficult, a rotary vacuum pump, the rotator running in oil, was used; this was similar to those used in evacuating incandescent lamps and afforded a pressure during distillation as low as one millimeter. Richards'[3] method of heating was used with excellent results, the current being regulated by wire and carbon rheostats. With a coil of platinum wire 0.25 mm. in diameter and 50 cm. long a current of 4–6 amperes at 220 volts was found sufficient to distil the hydrocarbons.

The distilling flask held but 200 cc., consequently many distillations were necessary. Six complete fractionations were made between the following temperatures, 95–100°, 100–110, 110–125, 125–130, 130–140, 145–150, 150–155, 170–176, 176–182, 186–193° and a quantity of each portion of fairly constant boiling point was obtained.

---

[1] THIS JOURNAL, 26, 665.

[2] *Ann. chim. phys.*, (3) 6, 40 (1842).

[3] T. W. Richards, THIS JOURNAL, 30, 1282.

The hydrocarbons were next subjected to purification by crystallization from acetone. Those having boiling points of from 95° to 135° would not separate out in crystalline form even at 0°, coming out of solution simply as oils; but the separation was repeated three times with these as with those of higher boiling point, since any change in composition which might be thereby affected tends toward purification. The remainder of the hydrocarbons were obtained as crystallized white solids from the acetone solutions, and crystallization from fresh acetone was effected three times in each case. The hydrocarbons which were last separated from the acetone were heated on the water bath to remove all traces of solvent. All except the one, crystallizing from acetone, which had the boiling point 130–140° were solid at the ordinary temperatures. The solvent was also distilled from the total mother liquor left from the three crystallizations leaving the hydrocarbon which is soluble in acetone at 0°. All of these soluble hydrocarbons, to the end of the list, were liquid at ordinary temperature.

By this means there were obtained, from the original single series of hydrocarbons, two series, one insoluble after three separations from acetone solution at 0°, and the other soluble in acetone at that temperature.

The molecular weights by the Beckmann method, in benzene, and the iodine absorption values by the Hanus method were now obtained for all the hydrocarbons of each of these series, both solid and residual; these are shown in Tables I and II.

TABLE I.—PURIFIED HYDROCARBONS.

Boiling points at 1 mm.	Molec. wts after 3rd recryst.	Corresponding to	Molec. wts. after 6th recrystallization.	Corresponding to	Iodine nos. after 3rd recryst.	Equal to atoms of iodine.	Iodine nos after 6th recryst.	Equal to atoms of iodine.
95–100°	239	Heptadecylene $C_{17}H_{34}$, 238,	oily, did not	....	87	1.6	..	...
100–110°	252	Octadecylene $C_{18}H_{36}$, 252,	crystallize	....	95	1.9	..	...
110–125°	287	Eicosylene $C_{20}H_{40}$, 280,	....	....	82	1.9	..	. .
125–130°	310	Docosylene $C_{22}H_{44}$, 308,	....	....	74	1.8	..	...
130–135°	318	Tricosylene $C_{23}H_{46}$, 322,	....	....	65	1.6	..	...
130–140°	324	Tricosylene $C_{23}H_{46}$, 322,	346	$C_{25}H_{50}$, 350	60	1.5	45	1.2
145–150°	354	Pentacosylene $C_{25}H_{50}$, 350,	378	$C_{27}H_{54}$, 374	57	1.6	43	1.3
[1]148°	348	Pentacosylene $C_{25}H_{50}$, 350,	....	....	60	1.7	..	...
150–155°	367	Hexacosylene $C_{26}H_{52}$, 364,	373	$C_{27}H_{54}$, 374	56	1.6	41	1.2
170–176°	392	Octacosylene $C_{28}H_{56}$, 392,	400	$C_{28}H_{56}$, 406	71	2.2	56	1.8
176–182°	410	Nonacosylene $C_{29}H_{58}$, 406,	412	$C_{29}H_{58}$, 406	72	2.3	67	2.2
186–193°	422	Triacontylene $C_{30}H_{60}$, 420,	424	$C_{30}H_{60}$, 420	80	2.7	72	2.4

[1] Of remarkably constant boiling point but insufficient to recrystallize.

TABLE II.—RESIDUAL HYDROCARBONS.

Boiling points at 1 mm.	Molec. wts. after 3rd recryst.	Corresponding to	Molec. wts after 6th recryst	Corresponding to	Iodine nos. after 3rd recryst.	Equal to atoms of iodine.	Iodine nos after 6th recryst.	Equal to atoms of iodine.
95–110°	Insufficient in quantity							
110–125°	284	Eicosylene $C_{20}H_{40}$, 280,	...	...	90	2.0	.	...
125–130°	305	Docosylene $C_{22}H_{44}$, 308,	...	..	85	2.1	..	...
130–135°	320	Tricosylene $C_{23}H_{46}$, 322,	...	...	80	2.1	..	...
130–140°	325	Tricosylene $C_{23}H_{46}$, 322,	332	$C_{24}H_{48}$, 336	83	2.1	66	1.7
145–150°	336	Tetracosylene $C_{24}H_{48}$, 336,	insufficient	....	79	2.1	.	...
150–155°	360	Hexacosylene $C_{26}H_{52}$, 364,	"	...	79	2.3	..	...
170–176°	366	Hexacosylene $C_{26}H_{52}$, 364,	395	...	86	2.5	70	2.2
176–182°	382	Heptacosylene $C_{27}H_{54}$, 378,	392	...	88	2.7	85	2.6
186–193°	402	Nonacosylene $C_{29}H_{58}$, 406,	409	...	93	3.0	96	3.1

From a study of these tables it would seem that in these distilled wool grease oleins we had hydrocarbons of the olefin series, that is with but a single double bond, and of formula from $C_{20}H_{40}$ to $C_{30}H_{60}$.

These hydrocarbons are now under investigation, with the idea of determining some of their physical constants with greater accuracy, more particularly their boiling and melting points, their index of refraction and, if possible, the position of the double bond.

BOSTON, MASS

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 177.]

STUDIES ON AMYLASES. I. AN EXAMINATION OF METHODS FOR THE DETERMINATION OF DIASTATIC POWER.

BY H. C. SHERMAN, E. C KENDALL AND E D CLARK.

Received June 28, 1910.

The enzymes being known by their activities it is scarcely possible to make satisfactory progress in the isolation of any enzyme for investigation of its chemical nature until we have accurate knowledge of methods and conditions for determining quantitatively the increase of its activity or power with the progress of the purification. This may be illustrated by a reference to the papers of Osborne[1] and of Wroblewski[2] on the chemical nature of the amylase of malt.

In the case of the amylases there are also extremely important applications, both biochemical and economic, awaiting the development of reliable and comprehensive methods for the measurement of diastatic power. The fact that the salivary digestion of starch may continue much longer in the stomach than was formerly supposed not only emphasizes the value of accurate measurements of the diastatic power of the saliva, but also adds interest to the use of both plant and animal amylases as aids to this part of the digestive process. The U. S. Pharmacopoeia standard for pancreatin has been changed so that the primary requirement now relates to amylolytic instead of to proteolytic power and recent food and drug legislation naturally suggests a more accurate standardization as well as a more comprehensive standard or standards which shall apply also to malt diastase and taka-diastase, both of which are likewise marketed as pharmaceutical preparations.

---

[1] Osborne, THIS JOURNAL, 17, 587 (1895); Osborne and Campbell, *Ibid.*, 18, 536 (1896); Osborne, *Ber.*, 31, 254 (1898).

[2] Wroblewski, *Ber.*, 30, 2289 (1897); 31, 1127 (1898).

Malt extracts are now being purchased by bakers on the basis of diastatic power and with the economic completion in the production of tax-free industrial alcohol it is to be expected that the determination of diastatic power will soon become an important factor in the valuation of commercial American malts.

In consequence of the very different points of view from which investigators have approached the subject of diastatic power, many methods or modifications of methods have been employed for its measurement and the descriptions are widely scattered in chemical, physiological, and technical literature. In the interest of brevity anything like a comprehensive review of such methods must be omitted here and attention confined to those which appear to have been most used.

These are of two main types: (1) the so-called "liquefaction" methods which aim to measure the power of the enzyme to completely convert a known amount of starch into products which no longer give the characteristic color reactions with iodine; (2) the saccharification methods which measure by means of alkaline copper solutions the amount of reducing sugar produced by the enzyme when acting under known conditions upon a sufficient excess of starch.

It will be convenient to refer to these two types as "iodine methods" and "copper methods" respectively.

Evidently the result obtained by either type of method will depend upon the conditions under which it is applied and further it may be expressed in a number of ways, for example, the amount of change produced by a given amount of enzyme in a given time, the amount of enzyme required to produce a given change in a given time, or the time required for a given amount of enzyme to produce a given change.

Kjeldahl[1] determined the reducing sugar formed by the action of a known amount of malt extract or saliva upon an excess of starch during 20 minutes at 57–59°, and considered that this was directly proportional to the amount of actual amylase present, or in other words, was a true measure of the diastatic power, so long as the digestion was not carried beyond the point which corresponds to a conversion of about 40 per cent. of the original starch into maltose. This is frequently referred to by other writers as "Kjeldahl's law of proportionality" and has had considerable influence upon subsequent work.

---

[1] Mittheilungen aus dem Carlsberger Laboratorium, *Dingler's Polytechn. J.*, 235. 379, 452 (1880).

Roberts[1] working with pancreatic extracts, saliva, and malt extract defined diastatic power as the number of cubic centimeters of a standard starch paste which could be converted by one cubic centimeter of the active solution during 5 minutes at 40° into products giving no color reaction with iodine.

Jungk[2] used a similar method for malt extract but determined the time required for 10 cc. of the extract to convert 10 grams of starch which he considered in the case of a good extract should not exceed 10 minutes at 40°.

Lintner[3] modified Kjeldahl's method in such a way as to ensure that the calculations of diastatic power should be based upon the production of a constant quantity of maltose by the action of the malt extract upon a definite amount of soluble starch. This was accomplished by measuring 10 cc. of a 2 per cent. starch solution into each of the several test tubes and adding to each tube a different amount of a malt extract, *e. g.*, 0.1, 0.2, 0.3, 0.4, 0.5 cc., etc. After standing for 1 hour at 21° the action was stopped by the addition of 5 cc. of Fehling solution to each tube, the tubes placed in boiling water for 10 minutes, and then examined to determine the first tube in which the copper was all reduced, *i. e.*, the smallest amount of extract which had produced sufficient maltose to reduce 5 cc. of Fehling solution. Lintner prepared a sample of diastase, of which 0.12 mg. produced under these conditions the maltose necessary to reduce the 5 cc. of Fehling solution. This preparation was rated as having a diastatic power of 100 and the diastatic powers of other preparations were calculated as inversely proportional to the amount of sample required to produce this fixed amount of reducing sugar. Thus, if 0.3 mg. were required $0.3 : 0.12 : : 100 : X \; . \; . \; . \; . \; X = 40$, the diastatic power of the preparation tested.

In applying this method to malt, however, 25 grams of the dried, ground sample are digested with 500 cc. of water and portions of the clear, filtered extract are employed as described for the diastatic solution. Then if V = the volume of extract required to give complete reduction of the Fehling solution

$$V : 0.1 : : 100 : \text{"diastatic power of malt."}$$

Since 0.2 gram starch are used in each test tube and the weight of maltose required to reduce 5 cc. of Fehling solution is only about 0.04 gram, it follows that the diastatic power is determined by this method for a point at which only about 20 per cent. of the starch has been converted into maltose. Hence the retarding effect of the maltose formed must act, if at all, to the same extent in all cases and so can not vitiate comparative determinations. On the other hand, if ten tubes containing 0.1 cc. to 1.0 cc. of the extract are used in testing a sample, there are only 10 points on Lintner's scale at which an accurate determination could be had in the first operation. If, as usually happens, the correct amount lies between the successive amounts taken, it is necessary to assume that the required volume is midway between the two, or to repeat the test with smaller increments of the extracts. Moreover, the probable error of the method increases rapidly with the diastatic power of the sample. If the end point falls between the last two tubes (0.9 cc. and 1.0 cc.) the diastatic power will be between 10 and 11.1, but if it falls between the first two tubes (0.1 cc. and 0.2 cc.) the diastatic power may be anywhere between 50 and 100.

---

[1] *Proc. Royal Soc.*, 32, 145 (1881); *J. Chem. Soc.*, 1881, 1051.

[2] *Am. J. Pharm.*, 55, 289 (1883), and *J. Chem. Soc.*, 46, 529 (1884).

[3] *Ztschr. ges. Brauwesen*, 1885, 281; *J. prakt. Chem.*, [2] 34, 378 (1886).

Kjeldahl,[1] Chittenden and Ely,[2] and later Brown and Glendenning,[3] Ford[4] and other investigators have estimated gravimetrically by copper reduction the extent of the diastatic action.

Sykes and Mitchell[5] introduced a method which they held to be interchangeable with Lintner's while giving a closer result in a shorter time, especially when dealing with malt of high diastatic power. In this method 100 cc. of 2 per cent. starch solution are treated with 1 cc. of malt extract or diastase solution (of the concentration used by Lintner) for 1 hour at 21°, 50 cc. of Fehling solution added, and the whole heated rapidly to 98° and then placed in a boiling water bath for 7 minutes, after which the reduced copper is determined. The weight of copper found, divided by 0.438 (the quantity of copper in 50 cc. of Fehling solution) and multiplied by 100, gives the diastatic power in terms of the Lintner scale. The results obtained by this method on 10 samples of malt having diastatic power of 5 to 77 (Lintner scale) averaged 2 units (about 8 per cent.) higher than those by the Lintner method with extreme variations of —1.7 to +5.8 units and of —34 to +30 per cent. This was accepted by Sykes and Mitchell as a satisfactory agreement of results.

Francis[6] improved the iodine method by extending the time of digestion to one-half hour, and specified exact conditions for the determination of the end point.

---

[1] *Loc. cit.*

[2] *Am. Chem. J.*, 3, 307 (1881–2).

[3] *J. Chem. Soc.*, 81, 388 (1902).

[4] *J. Soc. Chem. Ind.*, 23, 414 (1904).

[5] *Analyst*, 21, 122 (1896).

[6] *Bulletin of Pharmacy*, 12, 52 (1898).

Takamine[1] determines diastatic power in comparison with a permanent standardized sample of taka-diastase by finding the relative amount of the standard sample and the sample under test which are required to accomplish the same conversion in the same time as judged by the iodine color reaction.

Vernon[2] in his study of pancreatic amylase used a method essentially like that of Roberts.

Johnson[3] has recently published a new form of color method in which different amounts of the sample under examination are added to a fixed amount of starch paste, the mixture held at 40° and portions withdrawn and tested with iodine at the conclusion of 8 minutes and each minute thereafter. The operation is repeated with smaller increments of sample, if necessary, until that amount is found which just suffices to digest the starch in 10 minutes to products which give no color with iodine. Working mainly with samples containing commercial pancreatic amylase, Johnson concluded that diastatic values which were equivalent to each other as indicated by this method were also equivalent as measured by the production of reducing sugar.

The first object of our experimental work has been to ascertain, if possible, the relative value of some of the methods in use for measuring diastatic power, the consideration which should determine the choice of a method, what modification, if any, is necessary to ensure reliability of results, and how generally applicable is any one method to the examination of amylases of different origins. Much work having already been done by others upon malt diastase, we have confined our experiments almost entirely to taka-diastase and pancreatin.

In reaching the results given below we have been very greatly aided by the extended and able preliminary work on this subject which was carried out by the late Arnold William Meyer in conjunction with one of us in this laboratory in 1907–'08. We have also profited by the experience of Mr. Robert Schwarz and Miss M. I. Alley, who during the course of the investigation have carried out in this laboratory a considerable number of experiments on certain phases of the work.

Experiments upon Taka-diastase.

Three samples of taka-diastase have been used: No. 1, a one-ounce sample purchased in 1907; No. 2, a mixture of 4 one-ounce samples purchased in 1908; No. 3, a specially prepared sample of much greater activity which was kindly furnished us directly from the laboratory of Dr. Takamine.

---

[1] *J. Soc. Chem.'Ind.*, 17, 118, 437 (1898).

[2] *J. Physiol.*, 27, 174 (1901).

[3] THIS JOURNAL, 30, 798 (1908).

Lintner's method was carried out with all precautions which we had found suggested by any previous workers, using carefully prepared[1] and neutralized[2] soluble starch and neutralized[2] distilled water in specially cleansed Jena glass apparatus and working in a room kept free from laboratory fumes.

Taka-diastase No. 1 showed a diastatic power of 11.4 on Lintner's scale at 21° and 24.5 at 40°. No. 2 showed 7.8 at 21° and 17.5 at 40°. No. 3 showed 38.9 at 21° and 95.1 at 40°.

The gravimetric method showed with taka-diastase No. 1 (when 2.5 mg. of enzyme acted for 1 hour at 21° upon 100 cc. of 2 per cent. soluble starch) an amount of reducing sugar corresponding to a Lintner figure of 11.1. This result is in substantial agreement with that of the Lintner method. The difference between maximum and minimum in 9 successive determinations by this method was about 4 per cent. while in Lintner's method it was about 15 per cent., probably because of the errors involved in measuring out the very small amounts of enzyme solution required.

Johnson's method, while a great improvement over the Pharmacopoeia test, did not in our hands yield definite or satisfactory results because of the difficulty experienced, when following Johnson's directions, in securing a homogeneous starch paste and in determining the end point with sufficient accuracy.

A new iodine method seemed desirable which should differ from those of Roberts, Jungk, and Johnson in combining the use of a more dilute and homogeneous starch paste, a large volume of digestive mixture, and a fairly long time of digestion (as recommended by Francis) in order to secure a better mixture and more uniform action and diminish the proportional error involved in the determination of the end point.

The starch paste is prepared as follows: Enough clean air-dry potato starch to contain 10 grams of water-free substance is suspended in about 100 cc. of cold distilled water; enough more distilled water to make one liter was poured into a 2 to 3 liter flask immersed in a brine bath and connected with a reflux condenser. The bath is then heated and if the water boils the heating is stopped so that the water may cool somewhat, then the suspension of starch is poured *very carefully* into the hot water, the heating resumed and the paste boiled 2 hours under the reflux condenser. This long boiling renders the starch paste less viscous, more homogeneous and transparent, and more easy of digestion by the amylase.

[1] The small reducing power which the starch still retained after 65 careful washings on a Buchner funnel was determined and the proper correction applied.

[2] Rosolic acid was used as the indicator of neutrality in both cases.

In order to determine how long the boiling of the starch paste should be continued, experiments were made in which 250 cc. portions of the paste were treated with 40 mg. of taka-diastase No. 2 dissolved in 20 cc. of water and the time required for digestion to products giving no color with iodine was determined as follows: Boiled ½ hour, required 50 min.; 1 hour, required 46 min.; 1½ hours, 36 min.; 3 hours, 33 min.; 6 hours, 30 min. Hence boiling beyond 1½ hours had little effect upon the digestibility of the starch as thus determined. Moreover, it was noted that up to 2–3 hours the solutions remained colorless while on 3–6 hours' boiling they became slightly yellowish. Two hours was therefore decided upon as the best length of time for boiling the starch paste.

The paste at a temperature not above 40° is weighed out in 250-gram portions (equivalent to 2.5 grams anhydrous starch) into Erlenmeyer flasks of 350–400 cc. capacity and immersed in a water bath kept at 40°. The desired amount of enzyme is then introduced along with 20 cc. of water (in which the enzyme may be dissolved, or which may be used to wash it into the flask), the contents of the flask well mixed and the temperature of 40° carefully maintained. The digestion is considered completed when 0.25 cc. of the contents of the flask removed and mixed with 5 cc. of the dilute iodine test solution[1] in a test tube shows, when viewed against a white background, no color which can be distinguished from that of the untreated iodine test solution. The experiment is repeated with different amounts of enzyme, if necessary, until that amount is found which completes the digestion in 30 min. (± 1 min.). The result may then be conveniently expressed by dividing the weight of starch (2.5 grams) by the weight of enzyme required to digest it under these fixed conditions.

The results obtained with the three samples of taka-diastase were as follows, the times required with different amounts of sample being given to show the probable error of the method.

No. 1 — 37 mg. required 34 min., 40 mg. 27 min.; 43 mg. 22 min.; 38 mg. 31 min.

No. 2 — 40 mg. required 40 min.; 43 mg. 37 min.; 46 mg. 33 min.; 49 mg. 31 min.

No. 3 — 7 mg. required 34 min.; 9 mg. 30 min.; 11 mg. 27 min.

If the weight of starch, 2.5 grams, be divided in each case by the weight of taka-diastase which digested it in 30 or 31 min. the following values for diastatic power are obtained: No. 1, 66; No. 2, 51; No. 3, 278.

If these values be compared with the Lintner figures given above for the same samples at the same temperature we find the ratio of the Lintner figure to the value as found by the new iodine method to be for No. 1, 1 : 2.7; for No. 2, 1 : 2.9; for No. 3, 1 : 2.9.

---

[1] Two grams of iodine and 4 grams of potassium iodide are dissolved in 250 cc. water. For use, 2 cc. of this solution are diluted to 1 liter and 5 cc. of this dilute solution are employed for each test.

Hence as expressing the comparative diastatic powers of the three samples of taka-diastase, the results by the new iodine method ran approximately parallel to the results obtained by the Lintner method at the same temperature.

Experiments upon Pancreatin.

Five commercial preparations of pancreatic amylase representing the products of the principal American makers were used in the experiments here described.

The Lintner method was applied to these as to the samples of taka-diastase, but with much less satisfactory results. Duplicate determinations often showed wide divergence and lower results were obtained at 40° than at 21°.

The gravimetric copper method also gave unsatisfactory results. The amount of reducing sugar formed by a given amount of enzyme was less here than in Lintner's method and there was not a fixed relation between the amount of enzyme used and the weight of cuprous oxide formed.

Thus the 46 mg. of cuprous oxide in five cc. of Fehling solution were obtained in a Lintner test from 1.7 mg. of pancreatin. The same weight of pancreatin under the conditions of the gravimetric copper method gave only 14.4 mg. cuprous oxide, and increasing amounts of enzyme gave the following results:

Pancreatin, milligrams........	2.5	5.0	10.0	12.0	15.0
Cuprous oxide, milligrams....	27.0	62.8	202.6	270.0	379.0

In these experiments where only a small proportion of the starch was converted into maltose in any case, a given weight of pancreatin had a greater effect in 10 cc. than in 100 cc. of starch solution, while with different weights of pancreatin in the same volume (100 cc.) of starch solution the effect increased in greater proportion than the weight of pancreatin added. In both cases dilution appears to have injured the activity of the pancreatin.

The influence of dilution was studied directly by conducting experiments in pairs so arranged that the amounts of starch and enzyme and the conditions of time, temperature, etc., were exactly the same while the amount of water in which the action took place differed. At the end of the digestion enough water was added to the more concentrated solution to make the volumes the same for the determination of the reducing sugars which had been formed.

MILLIGRAMS CUPROUS OXIDE FROM REDUCING SUGARS FORMED BY 5 MILLIGRAMS ENZYME PREPARATION.

Enzyme and starch	In 55 cc	In 110 cc.
Taka-diastase No. 1, 2 grams starch	328	332
Taka-diastase No. 1, 4 grams starch	361	361
Pancreatin No. 1, 0.5 grams starch	170	115
Pancreatin No. 2, 3.0 grams starch	273	185
Pancreatin No. 4, 0.5 gram starch	110	68
Pancreatin No. 5, 0.5 gram starch	94	66

Here the taka-diastase produced the same effect when working in different amounts of water, but the pancreatins produced much less in 110 cc. than in 55 cc.—the activity of the pancreatic amylase was evidently diminished by its dilution with neutralized distilled water.

From these results and those above given it is evident that the diastatic power of pancreatic amylase was largely influenced by the ratio of amylase to water. Under these conditions, therefore, the testing of fixed amounts of commercial preparations containing varying amounts of actual amylase cannot be expected to give reliable results. This is because of the influence of electrolytes in activating the amylase.

In these experiments no electrolyte was added other than the small amounts of salts accidentally present in the soluble starch and the neutralized distilled water, hence there was insufficient electrolyte present either to fully activate the enzyme or to protect it from deterioration on standing in water solution. Hence the greater the amount of water present the less favorable the condition for enzyme activity. The optimum conditions as worked out for pancreatin and which permit of the accurate determination of its diastatic power by the grav metric method were not worked out until after our experiments with the iodine methods and will, therefore, be described later.

Johnson's iodine method gave us even less satisfactory results with pancreatin than with taka-diastase for the reason that as the digestion proceeds the test portions from the digestion mixture, when they no longer give a blue color with iodine, do give a red color which on continuing the digestion persists for a comparatively long time and disappears by almost imperceptible degrees so that it is extremely difficult to decide when the digestion should be considered finished.

The new iodine method showed in our experiments upon pancreatin the same advantages over Johnson's method as were noted in the experiments with taka-diastase, but still did not give a very satisfactory end point because of the rather long duration and gradual fading of the red color reaction. That the activity of the commercial pancreatin may be greatly increased by addition of a small amount of salt was shown almost as prominently by this iodine method as by the determination of the reducing sugar formed. Each of the four samples of commercial pancreatin tested digested 2.5 to 7 times as much starch under standard conditions in a solution containing 0.1 per cent. of added sodium chloride as in one to which no electrolyte was added. The stronger two preparations were tested in 0.3 per cent. salt solution and showed the same apparent activity as in the 0.1 per cent. solution.

By these and many other analytical data which must here be omitted for the sake of brevity, we became convinced that it is illogical and misleading to attempt to determine the diastatic power of pancreatin by its action upon pure starch in pure water because such a medium is too poor in electrolytes to permit the amylase to function normally, and that the conditions necessary for the amylase to function normally should be worked out and incorporated in the method to be used in the future for the determination of diastatic power. This led to a somewhat extended study of the action of pancreatic amylase the main results of which will be given in the next paper. The analytical procedure employed in that study and the optimum conditions for pancreatin as there found are included in the following description. Under these optimum conditions we obtain in testing commercial pancreatins results about 20 times as high as when no electrolyte is added.

PROPOSED GRAVIMETRIC METHOD.

Materials and Conditions.

Starch.—The starch for careful gravimetric work should be Lintner soluble starch, which gives a perfectly clear solution with boiling water. Ford[1] discusses very fully the preparation of such a starch. It should have a reaction with rosolic acid equivalent to less than 0.5 cc. of 0.01 normal acid or alkali per gram of anhydrous starch. In the anhydrous state it is quite hygroscopic; air-dry it contains about 15 per cent. of moisture. The lower the reducing power the better, but a reduction of 30 mg. of cuprous oxide per gram of anhydrous starch is not too large for accurate work.

Water.—The water used must be as nearly pure and as constantly uniform as is possible; redistilled and practicaly neutral to rosolic acid.

Temperature.—We prefer a temperature of 40° for all diastatic power determinations. This is obviously most suitable for the amylases of animal origin and there are important advantages and no important disadvantages in the use of the same temperature for the vegetable amylases. The solutions and flasks should be as near 40° as possible at the time of actually mixing the enzyme and the starch. The temperature should remain constant during the entire time of reaction, as a variation of one degree causes about 10 per cent. error in the result.

Time.—Since the time must in any case be somewhat arbitrarily chosen, we have decided upon 30 min. as best meeting the requirements of accuracy and convenience of working.

---

[1] *J. Soc. Chem. Ind.*, 23, 414 (1904).

Enzyme.—The enzyme may be dissolved in pure water if its power is to be tested immediately. If it is to stand, it should be dissolved in water containing 4 cc. of fiftieth-molar disodium phosphate per 100 cc. The test should be made within an hour in any case. The amount of enzyme to be weighed out will depend entirely on its strength.

One may dissolve the enzyme in a small amount of water and use a very small volume, or use a larger volume for the solution of the enzyme and measure larger amounts for the determination. We employed the former method, using a special 1 cc. pipette which was very accurately graduated. The actual weight of enzyme added to the starch solution varied from 0.1 to 1.0 mg.

Activating Agents.—These will doubtless differ with the different amylases. For pancreatic amylase acting on two per cent. starch, add 300 mg. sodium chloride and 7 cc. of fiftieth-molar disodium phosphate per 100 cc. (final volume) of reaction mixture.

Procedure.—Prepare 400 cc. of 2 per cent. soluble starch solution and the enzyme solution of such a strength that 1 cc. will contain from 0.4 to 1.0 mg. of enzyme. By means of a 1 cc. Mohr's pipette, accurately calibrated in hundredths, measure into four 200 cc. Erlenmeyer flasks such volumes of the solution as will contain 0.2, 0.5, 0.8, and 1.0 mg. of enzyme, respectively.[1] Now 100 cc. of the starch solution previously warmed to 40° is poured into each flask and the digestion allowed to proceed for 30 minutes, the temperature being accurately maintained at 40°. At the expiration of the 30 minutes, stop the reaction quickly by mixing at once with 50 cc. of Fehling solution and immerse the flask in a large bath of boiling water for 15 minutes. See that the water of the bath is kept boiling and that it stands above the level of the contents of any of the flasks. At the end of this heating filter quickly and determine the reduced copper by any accurate method. We prefer to filter through Gooch crucibles having thick felts of specially prepared asbestos, wash the cuprous oxide thoroughly with hot water, then twice each with alcohol and ether and weigh it as such after drying for at least 20 min. in a boiling water oven. The weight of cuprous oxide must not exceed 300 mg.

Correct the weight of reduced copper or cuprous oxide found for the reducing power of the soluble starch by subtracting from it the weight obtained in a "blank" test in which the starch solution is treated directly with the Fehling reagent.

Under the conditions here described the reducing power of maltose was found to be approximately the same as in Defren's method, so that the weight of cuprous oxide may be calculated to cupric oxide and the corresponding weight of maltose taken from Defren's table.

---

[1] The quantities suggested are such as were suitable for the pancreatins which we have tested. In testing other substances larger or smaller quantities may be necessary.

To express the results in terms somewhat comparable with those of Lintner's scale, multiply the weight of cuprous oxide by 0.2415, divide by the time in hours, and by the weight of enzyme preparation in milligrams. Results so obtained cannot, however, be considered as interchangeable with those found by Lintner's method because of the conditions of the determination and the form of the velocity curve of the reaction.

As will be more fully shown in the next paper, the rate of the amylolytic action is not constant up to a conversion of a considerable percentage of the original starch as Kjeldahl and others have held, but decreases as the conversion proceeds from the start, so that whatever the method of procedure the differing weights of cuprous oxide cannot be taken as standing in simple proportion to the actual diastatic power. However, if the velocity curve of the amylolytic action be plotted with time as abscissas and yield of reducing sugar as ordinates a scale may be established which will permit of an expression of true diastatic power based upon the weight of cuprous oxide obtained as above described. If 300 mg. of cuprous oxide be taken as 100 on such a scale the value on this scale of any lesser weight of cuprous oxide is obtained by expressing the abscissa corresponding to such weight as percentage of the abscissa for 300 mg. cuprous oxide. Calling the series thus obtained values of *K*, the diastatic power of the sample under examination is determined by dividing the value of *K* corresponding to the weight of cuprous oxide found by the number of milligrams of sample used to effect this conversion.

In the next paper in the consideration of the velocity of the reaction the mathematical relation between time and extent of conversion will be shown. From this relation an integral equation is deduced making it possible to establish this series by a mathematical means. The use of this equation verifies the experimental results and gives a convenient method for establishing values of *K*.

The accompanying table was constructed by finding the value for *K* from the equation for the action of pancreatic amylase upon 2 per cent. starch for every 10 mg. of cuprous oxide up to 300 mg.

VALUES FOR *K* FROM CUPROUS OXIDE FOUND.

Cuprous oxide. Mg.	*K*.	Cuprous oxide. Mg.	*K*.	Cuprous oxide. Mg.	*K*.	Cuprous oxide. Mg.	*K*.
30	9.1	100	31.2	170	54.1	240	78.3
40	12.2	110	34.4	180	57.5	250	81.8
50	15.3	120	37.6	190	60.9	260	85.4
60	18.4	130	40.9	200	64.3	270	89.0
70	21.6	140	44.2	210	67.8	280	92.6
80	24.8	150	47.5	220	71.3	290	96.3
90	28.0	160	50.8	230	74.8	300	100.0

In the equation, amounts of enzyme and time are reciprocal quantities. It is therefore evident that diastatic powers may still be compared when determined under different conditions of time as well as of amounts of enzyme employed.

The following example will illustrate how much more closely the results thus found correspond with actual amylolytic power than do the mere weights of cuprous oxide. In a set of determinations under uniform conditions 0.15, 0.30, 0.45, 0.60 mg of pancreatin yielded respectively 76, 147, 217, 286, mg. of cuprous oxide.

From the table we find the corresponding values of *K* to be 23.5, 46.5, 70.2, 94.8. Dividing these values by the respective weights of enzyme we obtain 156, 155, 156, 158. If we did not use the table, but divided the weights of cuprous oxide by three times the number of milligrams of enzyme, we would obtain 169, 163, 160, 159.

Furthermore, by application of this table, results obtained with different times of conversion may still be expressed on the same scale. With the proper activating agents present, any time of conversion from 15 minutes to two hours may be employed; and, if the amount of cuprous oxide does not exceed 300 mg., the results may be calculated as follows: Divide 30 (the standard time for the method described above) by the actual time of conversion in minutes, and multiply by the value of *K* as found in the above table. The product will equal the value which would have been obtained for *K* under standard conditions.

The procedure of the Lintner method may likewise be used and from the known weight of cuprous oxide in the tube in which the 5 cc. of Fehling solution is just reduced one may (after correcting for the reducing powers of the starch used) make use of the above table and express the results on the new scale of diastatic values.

Summary.

1. There seems to be no good reason for the diversity of conditions of temperature and time which have been given by different writers in the past, and it seems desirable that in all determinations of diastatic power the amylase be allowed to act at 40° and that 30 minutes be adopted as the standard time.

2. The Lintner method is sound in principle but does not prescribe optimum conditions, is not very delicate, and does not give a satisfactory degree of accuracy when applied to preparations of high diastatic power.

3. The gravimetric method as here described is capable of much greater accuracy and gives results which can either be stated in terms of cuprous oxide actually weighed, or of maltose, or in terms comparable with those of the Lintner scale, or on a new scale based upon the velocity curve of the reaction.

4. The new iodine method is believed to increase considerably the practicable accuracy of this type of determination and while it probably cannot be made as delicate as the improved gravimetric method, yet for those cases in which a satisfactory end point can be obtained, it has the practical advantage of simplicity and the theoretical advantage of marking the completion of a fairly definite step in the digestive process, whereas the copper reduction method measures the amount of a substance or substances produced by successive steps through intermediate products which are but imperfectly known.

5. With the three samples of taka-diastase examined, the end point in the iodine method was fairly satisfactory, consisting in a change from light blue to nearly colorless, and the results by the method were consistent with those by the Lintner method. It remains to be determined by examination of a larger number of samples under a variety of conditions whether the two types of method will give parallel results with taka-diastase throughout, or whether each method is capable of giving information which the other does not.

6. In the case of pancreatin, the iodine method does not seem capable of great accuracy because of the uncertainty in judging the point of change from a blue to a red reaction with iodine, and the comparatively long duration of the stage which gives the red color and which fades almost imperceptibly into the faint straw color of the iodine test solution itself.

7. With the copper reduction methods also, much more difficulty was experienced with pancreatin than with taka-diastase. In spite of all efforts to eliminate interfering impurities, irregular results were persistently obtained. This fact indicated the need of a detailed study of the action of pancreatic amylase, the results of which study are described in the paper which follows.

8. In the absence of added electrolytes the pancreatic amylase was so incompletely activated that it could not behave normally and was extremely susceptible to slight variations in the amounts of salts, acids, or alkalies accidentally present, so that the results were both misleadingly low and irregular. It is evident that in testing amylolytic power it is not the presence of electrolytes but their absence or insufficiency that constitutes the disturbing condition, and that reliable results are obtained only when the enzyme is properly activated so that it can function normally.

9. A gravimetric method is proposed which utilizes the results of a quantitative study of the action of pancreatic amylase, which study is described in the following paper. By this method, employing optimum amounts of salt and alkali for activation, we obtain in testing commercial pancreatins, results about 20 times as high as when no electrolyte is added.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 178.]

STUDIES ON AMYLASES. II. A STUDY OF THE ACTION OF PANCREATIC AMYLASE.

By E. C. KENDALL AND H. C. SHERMAN.

Received June 28, 1910.

In an examination of methods for the determination of diastatic power[1] it was found particularly difficult to obtain concordant results with pancreatin, and the peculiar behavior of the pancreatic amylase made plain the desirability of a special study of its action. The main results of this study are here given in as condensed and systematic a form as possible and not necessarily in the chronological order of the experiments.

Materials and Methods.

Enzyme Preparations.—In the experiments described in this paper the pancreatic amylase has been used in the form of commercial pancreatin. Seven samples purchased in New York City at various times during 1907–9 showed, when tested in the favorable conditions worked out during the investigation, the following relative diastatic powers: No. 1, 16; No. 2, 151; No. 3, 9; No. 4, 105; No. 5, 75; No. 6, 78; No. 7, 66. The stronger preparations which presumably contained the smaller amounts of impurities were used in the experiments described beyond.

Starch.—The soluble starch used was prepared by the Lintner[2] method with attention to the details discussed by Ford.[3] After completion of the acid treatment and removal of most of the acid by washing, the starch was transferred to a large glass bottle and washed about 65 times by decantation with about twice its bulk of water. At each washing the starch was vigorously mixed with the water by rolling the bottle back and forth on a table, after which the starch was allowed to settle thoroughly and the water siphoned off. This was repeated 3 or 4 times daily for about 3 weeks. The starch was then brought upon a Büchner funnel and the wash water removed as thoroughly as possible by suction, the slight acidity of the starch determined by titrating a weighed portion with $N/100$ alkali, using rosolic acid as indicator. The starch was then given a final washing with water containing the very small amount of sodium hydroxide calculated as necessary for its neutralization, filtered with thorough suction and air-dried. Four different preparations made in this way showed 12 to 17 per cent. of moisture, required 0.1 to 0.3 cc. of N/100 acid or alkali per gram for neutralization, and showed reducing powers of 27 to 30.5 mg. cuprous oxide per gram of anhydrous starch.

---

[1] Sherman, Kendall and Clark, THIS JOURNAL.

[2] *J. prakt. Chem.*, [2] 34, 378 (1886).

[3] *J. Soc. Chem. Ind.*, 23, 414 (1904).

Water.—Ordinary distilled water was found to be a cause of irregular results, especially when working without added electrolyte, nor did neutralization of such water render it satisfactory. In all subsequent work we used water which had been redistilled from alkaline permanganate, the steam being passed through a long column of glass wool to filter out any possible spray.

Procedure.—Unless otherwise stated the procedure was that of the gravimetric method for diastatic power proposed in the preceding paper except for the activating agents. The results are expressed in milligrams of cuprous oxide weighed, corrected for the reducing power of the particular soluble starch used in each experiment. In case it was impossible to determine at once the reducing sugars formed in an experiment, so that a means of stopping the enzyme action and preserving the solution was necessary, the addition of hydrochloric acid enough to make 0.1 per cent. stopped the action of the amylase at once and did not affect the reducing power of the solution, even on standing 24 hours. In cases in which the amylase acted more than one hour, a mixture of toluene and chloroform was added to prevent bacterial growth and evaporation. This was effective and had no influence upon the amount of copper reduced.

Influence of Added Electrolytes.

Neutral Salts.—As early as 1875, Nasse[1] held that there is an important and specific dependence of the activity of ferments upon the presence of salts. In his experiments the addition of chlorides, nitrates, and sulphates of sodium, potassium, and ammonium raised the diastatic power of pancreatin by 7 to 31 per cent.

Grützner[2] compared the effects of sodium chloride, bromide, iodide, and fluoride.

Vernon[3] found that pancreatic extracts suffered less loss of diastatic power when diluted with tap water than with distilled water and that the addition of a small quantity of salt increased the activity, and also diminished the reduction of activity occasioned by dilution. The activity of his preparation was 30 times as great in 0.1 per cent. salt solution as in distilled water.

Preti[4] reported that the amylases obtained from the pancreas, urine, blood serum, malt and cryptogams were all rendered practically inert by dialysis and restored to activity by the addition of a neutral electrolyte.

Bierry and Graja[5] working in conjunction with Victor Henri found a similar result with pancreatin.

[1] *Arch. ges. Physiol.*, 9, 138 (1875).

[2] *Ibid.*, 91, 195 (1902).

[3] *J. Physiol.*, 27, 174 (1901); 28, 156, 375 (1902).

[4] *Biochem. Z.*, 4, 1 (1907).

[5] *Compt. rend. soc. biol.*, 60, 479; 62, 432 (1906–7); *Compt. rend.*, 143, 300 (1906).

Slosse and Limbosch[1] also confirmed Preti's observations.

We have confirmed the observation that if both the pancreatin and the starch be first dialyzed in collodion sacks the pancreatic amylase becomes inactive but is reactivated by the addition of salt. Further experimentation showed that if the starch was dialyzed so that the only salts present were those of the enzyme preparation a small amount of high grade pancreatin was inactive; but was rapidly activated by the addition of very small amounts of salt.

Thus 0.35 mg. of pancreatin No. 2 in 50 cc. of 1 per cent. dialyzed starch at 40° for 1 hour showed after various additions of salt the activities indicated by the weights of cuprous oxide found as follows:

Sodium chloride milligrams .. .	0.01	0.1	1.0	10	30	60	90	121
Cuprous oxide milligrams... .	0	10	51	87	91	86	85	85

In another series of experiments 1 mg. of pancreatin No. 4 acted for 1 hour at 40° upon 100 cc. of 2 per cent. starch which had not been dialyzed with the following results:

NaCl. Mg.	Cuprous oxide Mg.	NaCl Mg.	Cuprous oxide. Mg.
0	13	60	183
0.1	34	100	182
0.5	90	200	182
1	119	400	167
5	171	600	168
10	178	800	158
20	186	..	..
25	180	..	..
30	187	..	..
35	193	..	..
40	194	..	..

Similar though less extended experiments upon four other samples of pancreatin gave confirmatory results.

If the enzyme preparation does not contain sufficient neutral electrolyte to completely activate the amylase, and no salt is added, a peculiar relation between rate of conversion and amount of enzyme is found. Doubling the amount of enzyme will more than double the rate of conversion, because doubling the amount of enzyme at the same time doubles the electrolyte in solution. Some results obtained with neutral solutions containing no added salt are:

Mg. Enzyme.	Mg. Cuprous oxide.
10	42
20	86
30	137
40	204
60	283
90	418

---

[1] *Bull. soc. roy. sci. med. nat. Bruxelles*, 1908, 80.

It is evident that salt not only helps the diastatic action but is essential to it. The salts accidentally present in commercial pancreatin and in very carefully prepared soluble starch are sufficient to enable the amylase to act to some extent, but any results so obtained are abnormal and entirely misleading as indications of real diastatic power, since pancreatic amylase acts in nature in a medium containing salt and must have an appreciable amount of some salt in order to function normally.

Experiments with potassium and ammonium chlorides gave similar results.

Alkalies.—Several investigators[1] of pancreatic and other amylases have reported alkalies harmful and some have found activity increased by the presence of a minute amount of acid, while others maintain that strict neutrality is the best condition for amylolytic action.

Tested without added electrolyte 5 mg. of pancreatin No. 5 acting upon 100 cc.[2] of 2 per cent. undialyzed starch for 1 hour at 21° gave the following results:

Cubic centimeters 0.01 N NaOH added. . .	0	1	2	3	4	6	8[1]
Milligrams cuprous oxide found .	71	61	49	42	24	14	4

These results were obtained by Meyer in the preliminary part of this study. No further experiments were made upon the influence of alkali alone because it was felt as already explained that any results obtained in the absence of sufficient salt to activate the enzyme must be regarded as abnormal.

Addition of Salt and Alkali.—Ebstein, in 1893,[3] showed that a degree of alkalinity which would otherwise stop the action of pancreatic amylase did not prevent a vigorous action when "blood salts" were present in the solution and this helpful influence of the blood salts appeared to be due chiefly to the sodium chloride. This observation does not seem to have been appreciated or followed up.

Our work has included a considerable number of observations of the same enzyme working in solutions containing sufficient salt but of varying alkalinity. In the following table are brought together results obtained at different times but which are fairly comparable in representing in each case the mg. of cuprous oxide reduced by the sugar formed from the action of 0.125 mg. of pancreatin No. 2 upon 0.25 grams of soluble starch[1] at 40° for the length of time stated.

---

[1] Chittenden and Ely, *Am. Chem. J.*, **4**, 107 (1882); Chittenden and Smith, Studies Yale Laboratory of Physiological Chemistry, **1**, 36 (1884–5); Duggan, *Am. Chem. J.*, **8**, 211 (1886); Schierbeck, *Skand. Arch. Physiol.*, **3**, 344 (1891–2); Ebstein, *Virchow's Archiv.*, **134**, 475 (1893); Wood, *Am. Chem. J.*, **15**, 663 (1893); Vernon, *J. Physiol.*, **27**, 174 (1901); Grützner, *Arch. Physiol.*, **91**, 195 (1902); Cole, *J. Physiol.*, **30**, 202 (1904); Effront, *Compt. rend. soc. biol.*, **57**, 234 (1904); Ford, *J. Soc. Chem. Ind.*, **23**, 414 (1904); Maquenne, *Compt. rend.*, **142**, 285, 1059 (1906).

[2] In these and all similar experiments the reaction volume stated was adjusted after the addition of acid or alkali and is therefore the total volume.

[3] *Virchow's Archiv*, **134**, 475.

EFFECT OF ADDED ACID AND ALKALI ON SOLUTIONS CONTAINING NEUTRAL ELECTROLYTE

Added acid or alkali.	Time.						
	10 min	30 min.	1 hr.	2 hrs	3 hrs.	5 hrs	25 hrs
8 cc 0.01 *N* H_2SO_4 per 100 cc			0		.	.	.
6 " " "			0		.		
4 " " "			3		7	..	..
3 " " "			87	151		222	277
2 " " "			153	218		251	272
1 " " "			223	242		254	271
Neutral			227	243		254	270
1 cc 0.01 *N* NaOH per 100 cc	143	207	235		240	252	..
2 " " "	156	204	226		244	250	
3 " " "	124	191	214		241	244	..
4 " " "			200	223	.	239	256
6 " " "			154	196		232	250
8 " " "			124	186		227	250
20 " " "			19		40	163	
30 " " "			11		18	40	
40 " " "			3		9	11	
50 " " "			0		4	6	

It will be seen from the data in the above table:

(1) That in solutions sufficiently acid, where the concentration of hydroxyl ion may be regarded as practically zero, there was no action; (2) that in passing from acid through neutral to faintly alkaline solutions the increasing concentration of hydroxyl ion is accompanied by an increased amylolytic activity up to the degree of alkalinity obtained by adding 2 cc. of 0.01 *N* sodium hydroxide per 100 cc. of solution; (3) that greater additions of alkali have a retarding effect but the action is not stopped except by the addition of relatively large proportions of 0.01 *N* solution; (4) that although the alkalinity of the solution has a great influence upon the speed of the reaction still there is a tendency toward a constant final yield of reducing sugar provided sufficient time be allowed.

In other experiments where a larger excess of starch was present the optimum amount of added alkali was found to be higher.

Experiments were also made in which varying amounts of sodium chloride and sodium carbonate were added. The following table shows the milligrams of cuprous oxide obtained by the action of equal amounts of pancreatin No. 2 upon equal volumes of 2 per cent. starch solution for 1 hour at 40°.

---

[1] One-half milligram pancreatin acted on 100 cc. of 1 per cent starch solution (containing the indicated amount of acid or alkali) of which 25 cc. were withdrawn and diluted to 100 cc. before treating with Fehling solution. The amount of added salt varied from 125–300 mg. and was sufficient in each case to activate the enzyme.

EFFECT OF ADDED SODIUM CHLORIDE AND SODIUM CARBONATE.

Sodium chloride. Mg.	Sodium carbonate, 00.1 N solution. 1 cc.	2 cc.	4 cc.	5 cc.	6 cc.	7 cc.	8 cc.	9 cc.	15 cc.
60– 100	234	248	280	290	284	278	250	244	84
120– 200	..	253	..	292	289	279	..	..	..
300– 400	..	..	..	290	291	278	256	261	96
500–1000	.	.	..	280	..	263	241	230	81

Comparison of these data with those previously given indicates that the amount of salt necessary to activate the enzyme is comparatively small (in none of these cases was it over 0.3 per cent.) and that moderate variations in the amount of salt added do not materially influence the optimum alkalinity so that even in alkaline solutions the helpful effect of the salt appears to be due to a direct activation of the enzyme rather than to its influence upon the ionization of the alkali.

If, however, the salt is insufficient to fully activate the amylase, the optimum alkalinity[1] rises with the concentration of salt. In a case of this sort the following results (expressed in mg. of cuprous oxide) were obtained:

EFFECT OF SALT UPON OPTIMUM ALKALINITY.

Added NaOH.	0.	1.	2.	3.	4.	5 cc. 0.01 N.
1 milligram NaCl	110	103	85	61	.	..
5 milligrams NaCl	214	243	233	202	..	..
500 milligrams NaCl	..	.	400	427	430	296

That the optimum alkali was higher here than in the preceding table is due to the fact that more starch was used. This relation will be fully explained later in this paper.

The results of some of the experiments made to compare the effects of different alkalis in the presence of a uniform amount of salt are shown in the following table.

As would be expected the optimum is reached more quickly and the retarding effect of excess is more pronounced with carbonate that with phosphate and with hydroxide that with carbonate. The activity at optimum concentration is, however, very nearly the same in all cases except with ammonia where the lower results may very probably be due to a solvent effect upon the cuprous oxide. It should also be noted that the unit of comparison is fiftieth-molar for phosphate while the hydroxide and carbonate solutions were 0.01 N by titration with standard acid.

---

[1] The above results show plainly the increase of activity produced by adding alkali in the presence of sufficient salt. Since Cole (*loc. cit.*) has shown that the activity of ptyalin is increased by acid it is suggested that some amylases may use the hydroxyl and others the hydrogen ion to accomplish the hydrolysis of starch. This point should be studied further upon other amylases sufficiently activated by salt.

The conditions for all these determinations were: One-half mg. pancreatin No. 4. Sodium chloride, 700 mgs. Temperature, 40°. Time, 60 min. Starch, 2 per cent.

EFFECT OF DIFFERENT KINDS OF ALKALI.

Alkali added.	Cuprous oxide, mg $NaOH$ N/100.	KOH N/100.	NH_4OH N/100	Na_2CO_3 N/100.	K_2CO_3 N/100	Na_2HPO_4 M/50.
None....	56	..	..	56	..	..
1 cc. 0.01 *N* per 100 cc.	153	.		132	..	.
2 " "	229	..	.	198	..	260
3 " "	279	280	255	242	.	.
4 " "	309	313	281	278	277	301
5 " "	307	289	273	290	.	
6 " "	196	151	206	301	302	304
7 " "	85	.		308	.	..
8 " "	49	.		314	297	306
9 " "		.		305	.	..
10 " "		.	.	273	222	313
11 " "				215	..	317
12 " "	..			159	..	304
13 " "	.	.		118	..	..
14 " "		.		102	.	305
15 " "		.		78	.	
20 " "		..		40	.	273
25 " "		..	.	29	..	..
30 " "				23	.	264
35 " "	..	.	.	18	.	..
50 " "	.	..	.	12	..	224
75 " "	.		.	9	..	..

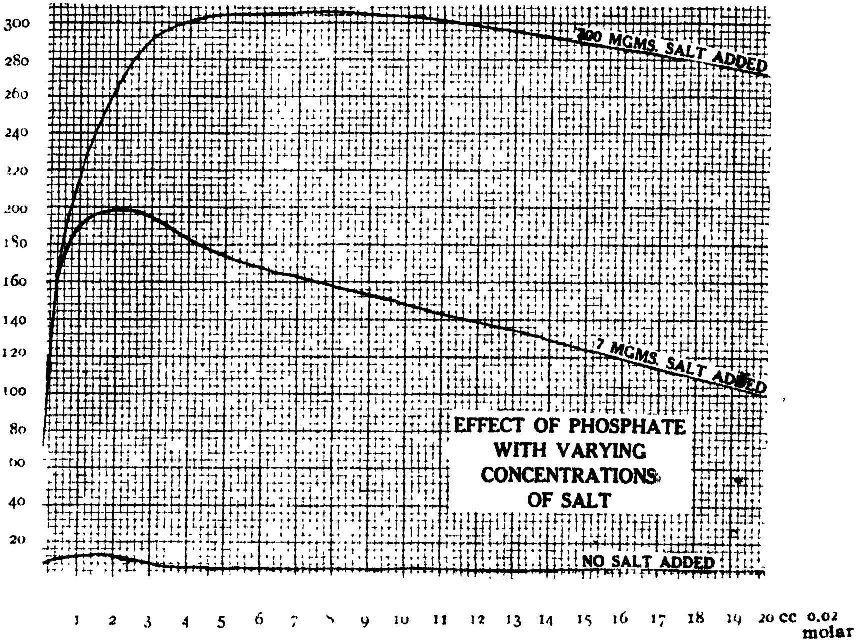
Disodium phosphate was also tried alone and with the addition of small and large amounts of sodium chloride. The weights of cuprous oxide obtained were as follows:

EFFECT OF PHOSPHATE AND DIFFERENT AMOUNTS OF SALT.

Cc. M/50. Na_2HPO_4.	Pancreatin No. 6, 10 mg. Added NaCl. None.	Pancreatin No. 4, 0.5 mg. Added NaCl 7 mg.	Added NaCl 700 mg
0...	161	72	51
1............ .	231	190	.
2........... ..	193	198	260
3.......... ...	159	194	.
4..............	..	182	301
5.....	118	..	..
6..............	..	163	304
8..............	..	150	306
20..............	53	100	273
30..............	..	77	264
40..............	35	69	236

Where no salt was added 20 times as much enzyme was used for the experiment in order to get a comparable yield of reducing sugar, hence the partial activation by the salts accidentally present.

Since the figures in one column are for a much larger weight of pancreatin than in the others, the effect may be more readily seen from the following curves:



When the phosphate alone was added in small amount it caused a rapid rise in speed of conversion but in slightly larger amounts its effect was depressing. At the optimum concentration of the phosphate alone the enzyme was very incompletely activated.

With the addition of a small amount of salt, sufficient largely, but not completely, to activate the enzyme, small additions of phosphate greatly increased the speed of the reaction while slightly larger amounts had a marked retarding action.

With the addition of an abundance of sodium chloride (0.7 per cent.) the phosphate continued to increase the speed of the reaction up to a much greater concentration, giving a maximum much higher than with the smaller amount of chloride, and beyond the maximum there was only a very gradual retardation as the additions of phosphate were still further increased.

The following results were obtained with 0.35 mg. of pancreatin 2, with 5 cc. of 0.01 normal sodium carbonate in 100 cc. of a solution of 2 per cent. starch.

EFFECT OF SALT ON THE TIME CURVE.

Time. Minutes.	Cuprous oxide with NaCl. 1.5 mg.	Cuprous oxide with NaCl. 5 mg.
20	12	21
40	23	42
60	33	66
80	44	88
100	56	111
120	68	133
140	79	154
160	92	178

Quantitative Relations of Enzyme, Starch Salt and Alkali.—In the experiments described in this paper we have usually employed (as will be seen from the descriptions accompanying the data) from 0.1 to 1 mg. of high grade commercial pancreatin. Our recent experiments upon the purification of pancreatic amylase give evidence that the pancreatin here used contained at least 90 per cent. of material other than actual amylase and as the volume has usually been 100 cc., we have a concentration not greater than 1 : 1,000,000 to 1 : 10,000,000 of actual amylase in the solution. Considerations of actual quantities relate, therefore, to starch, salt and alkali.

In discussing the influence of added salt and alkali, experiments have already been described in which the diastatic action was seen to rise rapidly at first with increasing concentrations of salt, after which a much greater increase of salt had very little effect. As further examples the following three pairs of determinations may be cited:

All other conditions being the same for the two tests in each set,

50 milligrams of salt gave 280 milligrams cuprous oxide.
1000 milligrams of salt gave 270 milligrams cuprous oxide.

100 milligrams of salt gave 84 milligrams cuprous oxide.
1000 milligrams of salt gave 81 milligrams cuprous oxide.

90 milligrams of salt gave 238 milligrams cuprous oxide.
2000 milligrams of salt gave 228 milligrams cuprous oxide.

It is also apparent from the table of results showing effect of added sodium chloride and sodium carbonate that the optimum alkalinity did not increase with increasing additions of salt. On the other hand there is an evident tendency to a higher optimum of alkalinity with an increasing concentration of starch. Thus 1.05 mg. pancreatin No. 2 acting for 20 minutes at 40° upon 100 cc. solutions containing 500 mg. salt and different amounts of starch and alkali gave the following results expressed in milligrams of cuprous oxide.

These results, as well as other data obtained under different conditions, including smaller and larger concentrations of starch, indicate that the amount of alkali to be added in order to obtain the most rapid conversion (*i. e.*, the optimum addition of alkali) increases with the concentration of the starch and that this optimum alkalinity is rather sharply defined for low concentrations of starch and becomes much less sharply defined as the concentration of the starch is increased.

Alkali added. Cc. of 0.01 *N* NaOH.	Starch, grams.			
	0.5	1 0	2.0	3.0
2	203	271	276	269
3	87	170	285	271
4	45	86	245	293
5	35	47	115	259

Thus the quantity of starch not only influenced the optimum of added alkali, but the enzyme was largely protected from the retarding effects of alkali in excess of the optimum by moderate increase in the concentration of the starch, whereas a proportionate increase in the amount of salt added had no noticeable effect.

Velocity and Equilibrium of the Reaction.

Influence of Concentration of Starch.—The following experiments bear upon the relation between amount of starch and the speed of its hydrolysis. Different amounts of pancreatin No. 6 were allowed to act at 40° upon a uniform volume (100 cc.) of starch solution whose strength was varied in the different cases from 0.1 per cent. to 4 per cent. In all cases 700 mg. of sodium chloride and 10 cc. of 0.02 molar disodium phosphate per 100 cc. of solution were added. The time of reaction was one hour. The figures are mg. of cuprous oxide reduced by the sugar formed under the given conditions.

Starch Per cent.	Pancreatin. mg.			
	0 15.	0.30.	0.45.	0.60
4	78	156	235	313
3	78	152	225	299
2	76	147	217	286
1	69	132	196	259
0.5	66	123	172	223
0.3	60	108	145	177
0.2	58	100	125	142
0.1	48	70	78	83

In another series the amount of starch present was so small that in no case was the increase in speed of conversion directly proportional to the weight of enzyme used, but it is seen that the rate of conversion is more nearly proportional to the enzyme in the higher concentrations of starch. The conditions were: Time, 5 minutes. Temperature, 40°. Disodium phosphate, 1.5 cc. 0.02 molar and sodium chloride, 200 mg. per 100 cc.

Starch. Per cent.	Pancreatin, mg. 0.1	0.2	0.3	0.4
0.1	12	19	28	35
0.2	12	19	28	37
0.5	12	23	33	41

It will be seen from the above tables that with sufficient amounts of starch the speed of conversion was directly proportional to the amount of enzyme present, while with less starch the increase in speed was not in proportion to the increase of enzyme. The sufficiency of the starch is not a matter of the percentage strength of the starch solution, but of the ratio of starch to enzyme. This point will be considered more fully below.

Influence of Alkalinity.—It has been pointed out that the effect of increasing alkalinity is, first to accelerate the speed of conversion and then to retard it. It has also been shown that the optimum alkalinity varies with the percentage of starch and for this reason the effect of a given amount of alkali on the time curve may be, first, acceleration, and then retardation. Therefore, if the time curve was determined, *e. g.*, for a solution of 2 per cent. starch containing the optimum concentration of alkali at the start, as the conversion proceeded, the alkali, which would remain constant, would have a greater retarding influence as its ratio to the amount of starch present increased.

If, on the other hand, the concentration of hydroxyl ion were much below the optimum at the start the speed of conversion would be greatly retarded, but as the action continued there would be a constantly accelerating influence (due to the diminishing percentage of starch) and finally the rate of conversion in this solution would equal, or exceed, that of solutions having a greater initial concentration of hydroxyl ion. The following data and chart illustrate this effect of alkali on the time curve, the results being given in mg. of cuprous oxide.

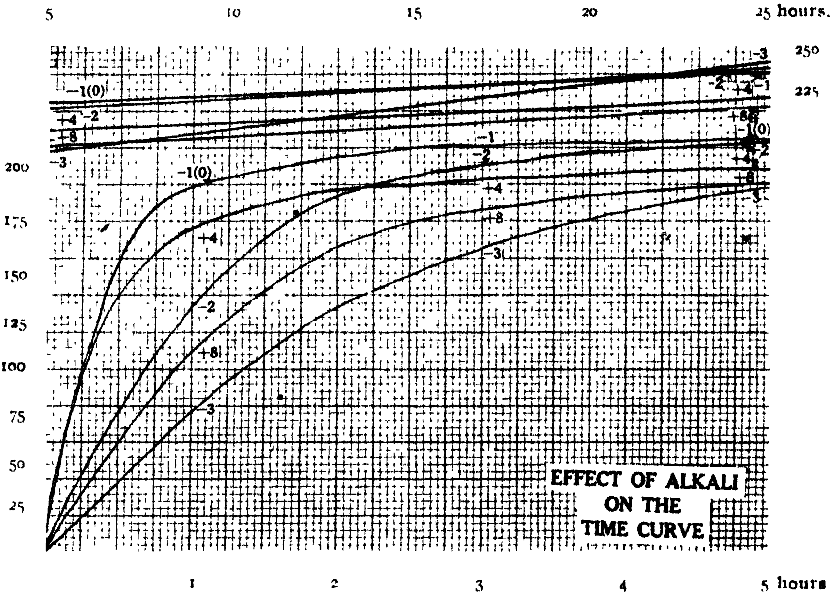
EFFECT OF ALKALI ON THE TIME CURVE.

Added acid or alkali.	Time, in hours. 1	2	5.	25.
3 cc. 0.01 *N* H_2SO_4	77	133	198	246
2 cc. 0.01 *N* H_2SO_4	135	193	222	242
1 cc. 0.01 *N* H_2SO_4	198	214	225	240
Neutral	201	215	225	238
3 cc. 0.01 *N* NaOH	199	212	218	230
4 cc. 0.01 *N* NaOH	177	196	211	227
6 cc. 0.01 *N* NaOH	136	173	205	221
8 cc. 0.01 *N* NaOH	109	165	201	221

The conditions for these determinations were: Starch, 1 per cent. Temperature, 40°. Volume (inclusive of added acid or alkali), 113 cc. Salt, 125 mg. Pancreatin No. 2, 5 mg.

This accelerating and retarding action of the alkali depending on the percentage of starch and therefore on the amount of conversion, explains one cause why previous investigators have found such varying conditions of alkali and acid for the optimum conversion of the starch.

An example taken from our work will show the great variation which may exist. When 4 per cent. starch was used and the time of conversion was limited to 20 minutes, 5 cc. of 0.01 *N* alkali per 100 cc. of solution were required for maximum speed of conversion. When 1 per cent. starch was used and 25 hours allowed for the time of conversion the greatest amount converted was in a solution containing 3 cc. of 0.01 *N* acid per 100 cc. of solution.



In discussing the curves we will designate the cc. of 0.01 *N* acid used as minus alkali; *e. g.*, —1, —2, or —3 will mean 1, 2, or 3 cc. of 0.01 *N* acid and +3, +4, +8 will mean cc. of 0.01 *N* sodium hydroxide.

The chart shows that a relatively high concentration of hydroxyl ion is required at first to give maximum speed to the reaction, but that a much lower concentration of hydroxyl ion will eventually cause the rate of conversion to equal, and finally exceed, that of the higher concentration. This is shown in the accompanying curves. At the end of 1 hour the amount of conversion is in the order 0, +3, —1, +4, +6, —2, +8, —3 cc. 0.01 *N* alkali. At the end of 5 hours the order is 0, —1, —2, +3, +4, +6, +8, —3, and at the end of 25 hours the order is —3, —2, — 1, 0, +3, +4, +6, +8.

The following set of determinations with varying amounts of alkali also illustrate this fact.

	5 min.	16 hrs.
0 cc. of 0.01 normal NaOH per 100 cc.	13	261
1 cc. of 0.01 normal NaOH per 100 cc.	15	251
2 cc. of 0.01 normal NaOH per 100 cc	17	245
3 cc. of 0.01 normal NaOH per 100 cc.	11	240

If we take the amount of the conversion in the first stages of the reaction we find the greatest speed in the solution containing 2 cc. of hydroxide per 100 cc., while after 16 hours the neutral solution shows the highest result.

A series of results where the time interval was less shows the effect of alkali in the first part of the conversion. The total time of digestion was only 5 hours, so the last set of figures does not represent the final equilibrium.

EFFECT OF VARIOUS CONCENTRATIONS OF ALKALI.

	Cc 0.01 *N* NaOH per 100 cc.			
Minutes.	0	1.	2	3
10.	124	143	156	124
20	185	195	194	177
30..	195	207	204	191
60	217	235	226	214
120	222	240	235	231
180.	229	241	244	241
240	231	248	246	243
300.	232	252	250	244

The conditions were: Temperature, 40°. 5 mg. of pancreatin 2. 300 mg. of sodium chloride per 100 cc. 1 per cent. starch.

Here, although the increments of alkali were very small, their influence was apparent throughout the five hours of the experiment.

To test the effect of a less caustic alkali sodium hydroxide and disodium phosphate were compared with the following results (expressed in mg. of cuprous oxide) in experiments on 1 per cent. starch containing 300 mg. sodium chloride per 100 cc.

Time. Minutes	With NaOH [1]	With Na_2HPO_4.[2]
5	48	49
10	85	88
15	119	124
20	145	151
25	164	170
30	174	180

The depressing effect of the alkali as the reaction proceeds is shown to be less with the phosphate than with the hydroxide.

---

[1] 2 cc. 0.01 *N* NaOH.

[2] 2 cc. 0.02 molar disodium phosphate.

Our results indicate that the point of final equilibrium in the conversion of starch by pancreatic amylase is but little influenced by variations in hydroxyl ion concentration within the limits which permit the action to take place with measurable speed. In the experiments already described in which the conditions varied from an addition of 3 cc. of 0.01 N H_2SO_4 to 8 cc. of 0.01 N NaOH the great difference of hydroxyl ion concentration was accompanied by a difference of only ten per cent. in the amount of reducing sugar found at the end of 25 hours.

In another series of experiments 10 mg. of pancreatin were allowed to act upon 4 grams of starch in 350 cc. of water containing 125 mg. salt per 100 cc. for about 16 hours. The solution was then divided into four equal parts, 5 mg. more of enzyme and the desired amounts of alkali were added to each part, and the reducing sugar found in the different flasks. The amount of conversion was found after the flasks had stood 1, 5 or 45 hours.

While the results do not agree exactly they show that there was no decided change in any of the flasks. The results are expressed in mg. of cuprous oxide.

	Cc 0 01 N NaOH per 100 cc.			
	0	10.	20.	30
When divided.	255	255	255	255
1 hour later	257	259	256	255
5 hours later	261	259	255	253

Another set with larger amounts of alkali gave:

	Cc. 0 01 N NaOH per 100 cc			
	20	30	40.	50
When divided	250	250	249	246
45 hours later	258	253	255	254

While there was a slight change in these solutions, still there was no decrease in reducing sugar to indicate reversion and within the limits of experimental error they all attained the same equilibrium.

Further, the equilibrium was not influenced by the amount of enzyme present. After standing 20 hours a solution containing 3 mg. of enzyme reduced 264 mg. of cuprous oxide and the same solution with 12 mg. of enzyme reduced 266. Two other solutions containing 3 and 12 mg. of enzyme reduced 246 and 249 mg. cuprous oxide respectively.

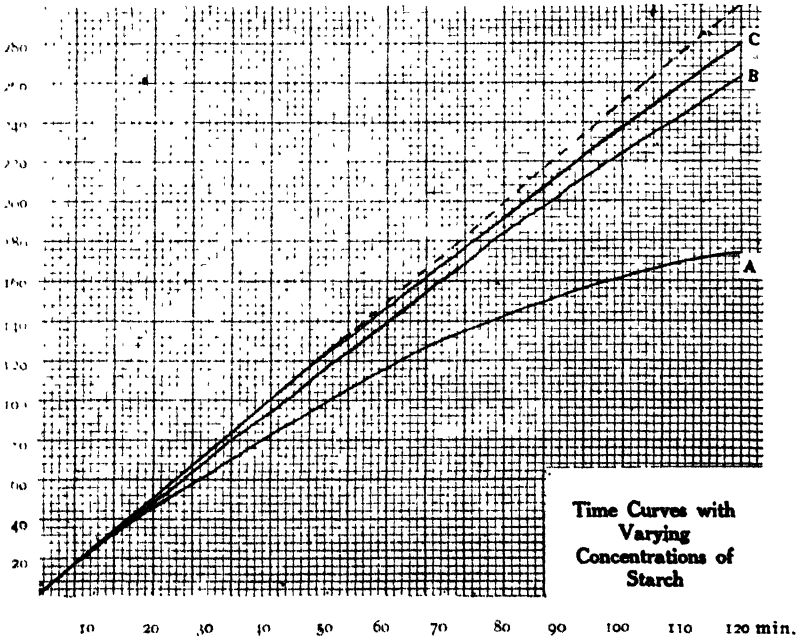
Velocity of Reaction.—Our principal data bearing upon the velocity of the reaction for different concentrations of starch were obtained in 4 series of experiments. In each experiment of the first 3 series (A, B, C) 0.6 mg. pancreatin No. 6 acted for the time indicated upon starch solutions the strengths of which were for series A, 0.5 per cent.; for B, 2 per cent.; for C, 4 per cent.; and which contained in all cases 700 mg. sodium chloride and 10 cc. of fiftieth-molar disodium phosphate per 100 cc. In series

D 5 mg. of pancreatin No. 2 acted upon 1 per cent. starch solution containing 700 mg. sodium chloride and 1.5 cc. of 0.01 *N* sodium hydroxide per 100 cc.

The results of the four series expressed in mg. of cuprous oxide were as follows:

Time. Min	Curve A.	Time Min.	Curve. B.	Curve. C	Time. Min.	Series. D.
20	47	10	25	25	5	81
40	83	20	48	50	10	140
60	117	30	72	74	15	172
80	142	40	94	100	20	184
100	160	50	118	125	25	194
120	174	60	138	147	30	198
140	179	70	160	170	40	204
160	187	80	185	192	55	212
180	189	90	204	215	70	214
200	193	100	224	237	100	221
220	197	110	243	259	130	225
240	199	120	263	280	190	230

The results of series A, B, and C are also shown graphically in the accompanying curves:



It will be seen from the data and curves (1) that the *initial* speed of conversion for a constant amount of enzyme was the same for the three different concentrations of starch; (2) that the speed of the reaction diminished more rapidly the smaller the initial concentration of the starch.

By a mathematical consideration of the relation between the original concentration of the starch and the amount of reducing sugar estimated as maltose formed, the following differential and integral equations were deduced:

$$\frac{dx}{dt} = K\left(\frac{C - x}{C + x} - \frac{x}{PC}\right)$$

and

$$\frac{PC(1-P+\sqrt{R})}{2\sqrt{R}M}\left(\log_{10}\frac{\sqrt{RC}+PC+C}{\sqrt{RC}+PC+C+2x} + \frac{\sqrt{R}+P-1}{\sqrt{R}-P+1}\log_{10}\frac{\sqrt{RC}-PC-C}{\sqrt{RC}-PC-C-2x}\right) = Kt.$$

In these equations:

C = original concentration of starch;

x = varying concentration of reducing sugar;

P = a constant;

R = $(P^2 + 6P + 1)$;

M = the logarithm of e to the base 10.

The value for P is determined by substituting the experimental results of series B and C in the equation and finding a number which gives constant values to K for the entire series of observations. The value thus found for P was 12. When the numerical data of our experiments were substituted for these letters the equation reduced to the form

$$\left(\log_{10}\frac{13.865\,C}{13.865\,C + x} + 6.9\log_{10}\frac{0.865\,C}{0.865\,C - x}\right) = Kt.$$

It is by means of this equation that the values of K given in the preceding paper were established.

Influence of Temperature.—Vernon[1] pointed out the fact that Roberts found an optimum temperature at 30°. The activity remained at its maximum until 45°, when it rapidly diminished to 70°, where it ceased. Vernon himself gives figures (with tap water) indicating 35° as the optimum temperature and the activity still existing at 65°. When he used 0.2 per cent. salt the results were widely different. The maximum activity was then at 50° instead of 35° C., but the action ceased between 65° and 70°.

Our results on the effect of temperature are as follows:

When no added electrolyte is present the effect of increasing the temperature from 21° to 40° is to depress the activity. The following Lintner figures were obtained with 4 samples of pancreatin:

Lintner figure		Per cent.
at 21° C.	at 40° C.	40°/21°.
6.98	5.78	83
1.27	1.16	91
13.79	12.22	88
1.38	0.83	60

---

[1] *J. Physiol.*, 27, 174 (1901).

If, however, the proper amounts of salt and alkali are present the activity at 40° is nearly four times as great as at 21°.

The following figures were obtained with pancreatin No. 6, by the regular gravimetric method followed throughout the work. There were 10 cc. of 0.02 molar disodium phosphate and 700 mg. of salt present in every 100 cc. of solution. One-half mg. of enzyme was allowed to act for 1 hour in each case.

Temperature.	Cuprous oxide Mg.
21°	65
30°	122
40°	238
45°	298
50°	345
55°	378
60°	256
65°	66

Between 20° and 40° the speed is about doubled every 10°, in accordance with van't Hoff's rule for normal chemical reactions; between 40° and 55° the acceleration is less, but temperature still has a great effect. Beyond 55°, where the maximum activity was obtained, the rate of change decreases very rapidly.

The depressing effect of increasing the temperature on amylase in solutions without added salt and alkali may be due to the fact that the water itself has a greater paralyzing effect at the higher temperature. We know that pure water, acting on pancreatic amylase free from neutral electrolyte, gradually destroys it, but if a trace of salt and alkali are present it will remain active for a long time.

Influence of Asparagine.—Marked differences of opinion exist as to whether asparagine really increases the diastatic power of amylases or only helps to give them favorable conditions for activity by regulating the reaction of the solution.

We have experimented upon the effect of asparagine in two ways:

First, by determining the time curve for solutions containing alkali with and without the addition of asparagine. The results of these showed no increase of activity in the presence of the asparagine.

The results are as follows:

	Cuprous oxide, mg.			
Minutes.	A.	B.	C.	D.
5	48	46	49	47
10	85	81	88	86
15	119	118	124	122
20	145	142	151	149
25	164	162	170	168
30	174	175	180	179

Solution A contained 2 cc. 0.01 *N* sodium hydroxide per 100 cc.
Solution B contained 2 cc. 0.01 *N* sodium hydroxide + 50 mg. asparagine.
Solution C contained 2 cc. 0.02 molar disodium phosphate.
Solution D contained 2 cc. 0.02 molar disodium phosphate + 50 mg. asparagine.

In a second series we added asparagine to solutions containing increasing amounts of alkali as phosphate.

So long as the amount of phosphate was below the optimum the addition of asparagine depressed the activity of the amylase. When so much phosphate was added that its alkalinity depressed the action, the addition of asparagine helped to counteract the effect of the excess of alkali and to allow the enzyme to act normally. The results follow:

Alkalinity of solution. cc 0.02 molar Na_2HPO_4 per 100 cc	Mg. cuprous oxide	
	without asparagine.	with asparagine.
2	260	227
3	(290)	281
4	301	291
5	(304)	309
6	307	312
7	(308)	327
10	313	329
16	296	329
20	273	324
30	264	316
40	236	307

In the presence of 10 cc. of 0.02 molar disodium phosphate increasing the amount of asparagine had no effect.

Asparagine. Mg.	Cuprous oxide. Mg.
10	321
100	329
150	328
200	330
300	324

Summary.

1. Pancreatic amylase when tested in the form of high grade commercial preparations upon soluble starch prepared by the Lintner method and purified by dialysis, was inactive, but was activated by the addition of a small amount of neutral electrolyte and was still further activated by the addition of both salt and alkali.

2. Until the enzyme was fully activated the optimum concentrations of salt and alkali appeared to depend upon each other; beyond this point the optimum concentration of alkali appeared to depend primarily upon the concentration of the starch.

3. With a given amount of enzyme, properly activated, the initial rate of hydrolysis was not dependent upon the amount of starch; as the re-

action proceeded its rate diminished but less rapidly the greater the amount of starch present.

4. Working with 1 per cent. starch, however favorable the conditions of salt and alkalinity and however large the amount of enzyme, the hydrolysis tended to come to equilibrium when the weight of maltose reached about 85 per cent. of the initial weight of starch.

5. In the presence of more than the optimum amount of alkali the point of equilibrium was approximately the same if sufficient time was allowed and fresh enzyme added during the reaction.

6. The data obtained have been applied in a method of determining and expressing diastatic power based upon the optimum conditions of salt and alkalinity as found for pancreatin and the quantitative relation between the amount of amylase and the reducing sugar it produces as shown by the velocity curve. The description of this method has been given in the preceding paper.

7. Between 20° and 40° the action of pancreatic amylase (properly activated by sodium chloride and sodium phosphate) showed a temperature coefficient approximating van't Hoff's rule for normal chemical reactions, since it nearly doubles for a rise of 10°.

8. Tested in solutions of varying alkalinity containing sodium chloride and sodium hydroxide or sodium phosphate, asparagine showed little, if any, effect not explainable by its influence upon the alkalinity of the solution.

NOTE.

Note: Preparation of ortho- and para-Nitrophenols.—The preparation of the nitrophenols as ordinarily carried out is accompanied by the production of much tar and is a somewhat unpleasant operation. The yield of the para compound is small, 50 grams of phenol giving according to Gattermann only from 5 to 10 grams of para-nitrophenol. Inexperienced operators often get no more than one or two grams of the compound, if any at all. This justifies the publication of the improvement recommended in the present note.

The production of tar is completely avoided and a yield of 18 per cent. of para-nitrophenol (13 grams from 50 grams of phenol) is obtained uniformly, *if the nitric acid is vigorously stirred during the addition to it of the phenol.* The results given below were obtained by carrying out the operation as follows: A solution of 80 grams sodium nitrate and 100 grams of strong sulphuric acid in 200 cc. of water was energetically stirred with the aid of a small water motor and kept at about 25°. To this was added drop by drop, at the rate of about 30 or 35 drops a minute, out of a separatory funnel, a solution of 50 grams crystallized phenol in 5 grams alcohol. The stirring was continued for about one-half hour after the addition of the phenol was completed, the mixture was allowed to stand for an hour and one-half longer, and then treated, as usual, with double its volume of water. The heavy oil that separated out was reddish-brown in color, but invariably transparent and free from sticky or tarry ingredients. The oil was washed two or three times with water and subjected to distillation with steam. The distillate yielded slightly less than 30 grams of a beautiful ortho-nitrophenol (the quantity obtained by Gattermann). The residue was evaporated to less than half its volume, boiled with 20 grams of bone-black, filtered hot, and allowed to crystallize in the cold. Two consecutive operations yielded, respectively, 13.2 and 12.9 grams of pure para-nitrophenol, which is about 18 per cent. of the theoretical yield from 50 grams of phenol. A nitration similarly carried out, but with the temperature kept, not at 25° but at 4°, resulted in 12.8 grams of para-nitrophenol. Below 4° the nitration refused to take place, altogether. Further, a nitration carefuly carried out at 50° yielded 12.5 grams of para-nitrophenol and slighty less of the ortho compound than is usually obtained at lower temperatures.

The temperature thus seems to have but little influence on the yield of both ortho- and para-nitrophenol, and the ordinary temperature of the laboratory is but slightly more propitious than either higher or lower temperatures. Far more important are the vigorous stirring of the solution during nitration and the very gradual addition of the phenol.

R. S. HART.

CLARK UNIVERSITY, WORCESTER, MASS.,
June 18, 1910.

NEW BOOKS.

Radiochemistry. By A. T. CAMERON, M A., B.Sc., Lecturer in Physiological Chemistry, University of Manitoba. London: J. M Dent & Sons, Limited 1910. viii + 174 pp. Price 2 s. 6d. net.

The book, the contents of which are based largely on three articles dealing with the "Transformation of Elements" which appeared in *Science Progress* in 1908, treats selected topics of the subject of radioactivity from the chemical point of view. The physical side is sketched only in sufficient outline to enable the reader who has some knowledge of physics and chemistry to appreciate the chemical results.

Those chapters which recount the properties and chemical behavior of radium emanation are of greatest interest; part of the results represent the author's own work with Sir William Ramsay. Radium emanation is now known in the solid and liquid as well as in the gaseous state. In the latter form it is produced to the extent of 0.1 cm. per day per gram of radium. The liquid emanation has a density of about 5; it boils at

—62°; it is practically colorless, with a marked greenish phosphorescence; the solid glows with great brilliancy like a small steel-blue arc light. It is now fully established that the emanation can bring about numerous purely chemical reactions; "each atom of the emanation, as it disintegrates, produces a certain definite chemical effect." It is also certain that helium is a product of the spontaneous disintegration of the emanation; but the possibility of the transmutation or atomic degradation of common elements under the influence of the emanation is still an open question. In addition to the familiar case of copper and lithium, these supposed transmutations now include the production of neon from the emanation and pure water, argon from a copper solution, and carbon dioxide from each of the elements thorium, zirconium, lead, titanium and silicon. However, the author shows that it is possible that the lithium came from the glass, in which it previously existed and that the neon and argon came from the air, while the carbon dioxide may have been formed by purely chemical changes of traces of carbonates present as impurities. (Although thorium oxalate is by far the least soluble of all oxalates, the reviewer has observed that it is appreciably soluble in a concentrated solution of thorium nitrate. Since thorium is always separated as oxalate in the process of manufacture, it is possible that some oxalate may remain in the otherwise pure nitrate and by subsequent decomposition give carbon dioxide.) The last two chapters are devoted to applications of radioactivity to geology and to medicine; a bibliography of nearly one hundred titles completes the book.

For a greater part of the matter of the second chapter, which treats of radioactive methods as illustrated by the thorium series, acknowledgement is made to Rutherford's *Radioactivity*, second edition. But apparently the author has not read this classic very carefully, if we may judge by pp. 16–18. In explanation of the rise to a maximum of the activity of the Th X separated from Th, it is said that this maximum represents the time when in any given interval as much of the products of Th X is formed as decays in that time. "These products are then said to be in radioactive equilibrium and no longer affect the nature of the curve." Now, as a matter of fact, the maximum *amounts* of the products are not reached until about 40 hours after the start, whereas the maximum *activity* is attained in about 18 hours. Furthermore the decay curve, as measured by the activity, is appreciably affected for three days after the maximum activity is passed and at no time does a state of radioactive equilibrium result. In giving the fundamental equation for the decay of any radioactive substance, p. 17, the author has blindly followed the misprint in Rutherford, p. 222, writing $I_0/I_t = e^{-\lambda t}$, instead of $I_t/I_0 = e^{-\lambda t}$. This leads him to the erroneous equation $2 = e^{-\lambda t}$, where t is now the period. On p. 90 the same incorrect fundamental equation occurs twice. A number of other errors occur; as p. 26, that the δ rays obey the light laws; p. 39, that U X dissolves in the *ether* layer, in the separation by Crookes' method and p. 55 that thorium occurs chiefly in Ceylon. However, the story of radioactivity is inherently so interesting that, in spite of these errors, the book will not disappoint the reader who wishes to learn the present state of our knowledge of radioactive transformations and suspected transmutations.

HERBERT N. MCCOY.

Outlines of Organic Chemistry. By F. J. MOORE, PH.D., Associate Professor of Organic Chemistry in the Massachusetts Institute of Technology. New York City: John Wiley & Sons. 1910. pp. ix + 315. Cloth, $1.50.

The book is the outgrowth of a series of lectures given to students whose principal work is in Physics, Biology and Sanitary Engineering. It differs from most elementary texts in that a few of the customary subjects are omitted and in those subjects considered only a few compounds are taken up, but these are discussed fully and clearly. Its aim seems to be "to teach not much but well." The almost complete absence of empirical formulas is noticeable.

Typographical errors incident to a first edition are found in formulas on pages 47, 94, 159 and 184. Most teachers of chemistry will object to oxidation or reduction reactions being written with the symbols O_2 or H_4 where ordinary oxidations or reductions are being described, pages 112, 251, 254, 261, 264, 266, 272, 281, 284 and 293. The formula for an isocyanide, page 74, and the spelling of the plural of formula, page 84, should be changed to agree with modern chemical usage.

Organic chemistry is being recognized as a subject of general interest and for the needs of the average students in the short courses, which are being given in increasing numbers by the American colleges and universities, this text will be found to serve excellently.

RALPH H. MCKEE.

Handbuch der landwirtschaftlichen Bakteriologie. By DR. F. LÖHNIS. Berlin; Gebrüder Borntraeger. 8vo. viii + 907 pp.

The development of agricultural science, like that of any other science, is marked by the appearance, from time to time, of books that summarize and interpret the data scattered in current publications. The present volume may be deservedly included in this list of important books, both for the unusual richness of the reference material contained in it and for the scholarly interpretation of the almost endless array of facts dealing with some of the agricultural relations of bacteria.

The five divisions of the book are arranged as follows: (1) Occurence and Activities of Microörganisms in Foodstuffs, 97 pp.; (2) Occurrence and Activities of Microörganisms in the Retting of Flax and Hemp and in the Fermentation of Tobacco, 16 pp.; (3) Occurrence and Activities of Microörganisms in Milk and Milk Products, 310 pp.; (4) Occurrence and Activities of Microörganisms in Barnyard Manure, 73 pp.; (5) Occurrence and Activities of Microörganisms in the Soil, 280 pp; Index, 115 pp.

No attempt is made by the author to discuss the bacteriology of water, sewage and sewage disposal. Evidently these topics appeared to him as belonging properly to the domain of sanitation, rather than that of agriculture. Similarly the rather extensive body of facts relating to bacteria pathogenic to higher plants is not considered by the author. While this may appear unfortunate to some of us, it must be admitted that he had good reason for this omission, since any discussion of plant-pathology from the bacterial standpoint alone must of necessity remain incomplete and one-sided. To secure completeness, one would have to consider the more or less distinct field of mycology, a task that would be hardly pertinent and far from simple.

To the American student this volume will prove of especial interest, because of the very satisfactory review of American data. The author deserves much credit for the thoroughness of this part of his work, particularly since he had to depend for his material almost entirely on the Experiment Station Record. Incidentally this achievement may be regarded as a splendid compliment to the editor and staff of the Experiment Station Record. For instance, the reference material on ensilage; on the numbers and kinds of bacteria in milk as influenced by handling and treatment; and on the ripening of hard and soft cheeses is reasonably complete. The same may be said of much of the soil-bacteriological work of the Delaware, North Carolina and New Jersey Experiment Stations.

Everything considered, the Handbook should prove serviceable to every student, teacher and investigator in the domain of agricultural bacteriology. All of these will feel indebted to the author for the many hours of tedious searching in books and journals that he will have saved them. They will, no doubt, appreciate also the helpful discussion of methods and culture media that represents one of the valuable features of the book. JACOB G. LIPMAN.

Laboratory Exercises in General Chemistry. WILLIAM MARTIN BLANCHARD, Professor of Chemistry, Depauw University. The Chemical Publishing Company: Easton, Pa. pp. 88. Price, $1.00.

This is a laboratory manual in general chemistry "arranged to meet the needs of college students who have had no previous training in chemistry." While there is little original material in the book, the experiments are well chosen and carefully written and include a number of quantitative experiments. To perform those given will require about six hours a week during the college year. C. W. BALKE.

RECENT PUBLICATIONS.

ACKERMANN, E.: **Dictionary of Portuguese Mining Terms, with French, English, and German Equivalents.** London: The Mining Journal, 8 s.

ANDRÉS, L. E.: **Der Kesselstein, seine Entstehung und Verhütung.** Wein: A Hartleben, 4.80 M.

ARENDT, R.: **Grundzüge der Chemie und Mineralogie.** 10, vermehrte Auflage, von L. Doermer. Hamburg: 8°, 539 pp., 4.60 M.

ASHLEY, H.. **The Colloid Matter of Clay and its Measurement.** (Bulletin U. S. Geological Survey). W. Wesley, 65 pp., 3 s.

ASKENASY, P.: **Einführung in die technische Elektrochemie.** Braunschweig: 251 pp., 10 M.

BARTHEL, C.: **Methods Used in the Examination of Milk and Dairy Products.** Macmillan: 8°, 272 pp., 7 s., 6 d.

BECKURTS, H.: **Dei Methoden der Massanalyse.** Unter Mitwirkung von O. Lüning. (2 Abteilungen). Abetilung I. Braunschweig: 8°, pp. 1-482, 14 M.

BIEDERMANN: **Die Sprengstoffe, ihrer Chemie und Technologie.** Leipzig: B. J. Teubner, 1.25 M.

BUJWID, O.. **Mikrophotographischer Wandatlas der Bakteriologie.** Berlin· Oscar Rothacker, 60 M.

CAMERON, A. T.· **Radiochemistry.** London: J. M. Dent & Sons. 8°, 184 pp., 2 s., 6 d.

CAPAUN-KARLOWAS: **Chemisch-technische Spezialitäten und Geheimnisse mit Angabe ihrer Zusammensetzung nach den bewährtesten Chemikern.** 5. Auflage von M. v. Waldheim. Wien: A. Hartleben, 3.30 M.

CETTOLINI, S.: **Distillazione del vino ed utilizzazione dei residui della vinificazione.** Vol. II. Mailand: F. Vallardi, 16, 419 pp., 4 L.

Dal mosto al vino, La fermentazione alcoolica. Mailand: U. Hoepli, 16, 490 pp, 4.50 L.

CHARTIER, M.: **Etude sur la production du Caoutchouc dans les Colonies Françaises.** Paris: 8°, 162 pp.

Chemische Technologie der Neuzeit. Bearbeitet von K. Arndt, E. Börnstein, E. Valenta u. a., herausgegeben von O. Dammer. (3 Bände in 12-13 Lieferungen). Stuttgart: 8°, Jede Lieferung, 6 M.

CHESNEAU, G.: **Theoretical Principles of the Methods of Analytical Chemistry Based upon Chemical Reactions.** New York: Macmillan, 184 pp., $1.75.

CLARKE, F. W.: **A Recalculation of the Atomic Weights.** Third edition. Washington: Published by the Smithsonian Institute.

COUTURAT, L., LORENZ, R., UND OSTWALD, W.: **International Language and Science.** London: Constable & Co.

CUSHMAN, A. S., AND GARDNER, H. A.: **The Corrosion and Preservation of Iron and Steel.** New York: McGraw-Hill, 373 pp., $4.00.

DUHEM, P.: **Thermodynamique et Chemie.** Leçons elementaires. Second edition. Paris: 8°, 592 pp., 13 M.

Ergänzungstaxe zur Deutschen Arzneitaxe für 1910, hrsg. v. Deutschen Apotheker-Verein und in dessen Auftrage bearb. von H. Stein. Berlin: 8°, 241 pp., 2.50 M.

EULER, H.: **Algemeine Chemie der Enzyme.** Wiesbaden: 8°, 241 pp., 7.60 M.

Farrell, F. J.: **Dyeing and Cleaning.** A Practical Handbook. A. Griffen, 8°, 252 pp., 5 s.

Fleck, C: **Photokeramik.** Anleitung zur Übertragung photographischer Aufnahmen auf Porzellan, Emaille, Glas, Metall. Berlin. G. Schmidt, 1.20 M.

Fleming, L. A. **Practical Tanning.** A Handbook of Modern Processes, Receipts, Suggestions, Etc. Philadelphia: H. Cary Bird & Co., 8°, 630 pp., $6.00.

Franke, G. **Handbuch der Brikettbereitung.** 2 Bd. Die Brikettbereitung aus Erzen, Huttenerzeugnissen, Metallabfallen u dergl., einschl. der Agglomerierung. Stuttgart· Ferd Enke, 8°, 216 pp., 9.40 M

Guareschi, R.· **Fermentazione e fermenti.** Mailand. U. Hoepli, 16, 350 pp, 3 L.

Gumbrecht, O.: **Wie studiert man Chemie und die beschreibenden Naturwissenschaftenc** 3 Aufl. Leipzig: Arthur Rossberg, 1 M.

Handbuch der deutschen Aktien-Gesellshaften. Berlin. Verlag für Borsen-und Finanzliteratur, 22 M.

Hell, G.· **Pharmazeutisch-technisches Manuale.** Bd. I. Pharmazeutischer Teil. 5 vermehrte Aufl. Wien: Urban & Schwarzenberg, 16.20 K., Bd II. Aufl., 16 20 K.

Herzfeld, J **Das Färben und Bleichen von Baumwolle, Wolle, Seide, Leinen, Etc.** Second edition. (3 Teile). Teil 3. Praxis der Farbeuei (10 Lieferungen). Berlin· 8°, Jede Leiferung, 1 M.

Holleman, A F.: **Die direkte Einführung von Substituenten in den Benzolkern.** Leipzig: Veit & Co, 8°, 20 M.

Hopkins, C. G **Soil Fertility and Permanent Agriculture.** Boston: Ginn & Co, 653 pp, $2.75.

Humphrey, R.· **The Fire-Resistive Properties of Various Building Materials.** (Bulletin U S. Geological Survey). W. Wesley, 8°, 99 pp., 3 s.

Johnson, J P **Ore Deposits of South Africa.** New York Henley, $2.00.

Kietaibi, K **Das Generatorgas. seine Erzeugung und Verwendung.** Wien: A. Hartleben, 4.80 M.

Lauber, E.: **Praktisches Handbuch des Zeugdrucks.** II. Suppl. Bd I. Jahrg. hrsg. von A. Sansone Leipzig: Gustav Fock, 9 u. 10 Lfg, je 2 M

Lewis, E. J. **Qualitative Analysis Tables for Use at the Bench.** Cambridge: University Press.

Mäkelt, E.· **Die Stromerzeugung durch fallende Teilchen in Flüssigkeiten und der absolute Nullpunkt des Potentials.** Dissert. Leipzig: Julius Brandstatter, 98 pp.

Meyer, D.: **Die Kalk und Magnesiadüngung.** Berlin· Paul Parey, 2.50 M.

Mittelstaedt, O.: **Technical Calculations for Sugar Works.** New York: Wiley, 12,° 117 pp., $1.50.

Moeller, J., und Geisler, E.: **Real-Enzyklopädie der gesamten Pharmazie.** Berlin: Urban & Schwarzenberg.

Neumann, A.: **Analyse und Antidote der für den Arzt wichtigsten Gifte.** Berlin: Berlinische Verlagsanstalt, 1.25 M.

Radford, W. A.: **Cement and How to Use it.** Radford Architectural Co., 8°, 369 pp., $1.00.

Rabow, S.: **Arzneiverordnungen 1910.** 41 Aufl. Strassburg: Friedrich Bull., 2.40 M. **Die neuesten Arzneimittel und Spezialitäten.** 2 Aufl. Strassburg: Ludolf Beust.

ROBERTSON, W. G.: **Manual of Medical Jurisprudence, Toxicology and Health.** 560 pp., 8 s.

SPETER, MAX.: **Lavoisier und seine Vorläufer.** Stuttgart: Ferd. Enke.

THOMPSON, S. P.: **The Life of William Thompson, Baron Kelvin of Largs.** 2 Bde. New York: Macmillan, 1297 pp., $7.50.

TREADWELL, F. P.: **Quantitative Analysis.** Translated by W. T. Hall. Second edition. New York: Wiley, 8°, 787 pp., $4.00.

WAIDNER, C. W., AND BURGESS, G. K.: **Platinum Resistance Thermometry at High Temperatures.** Washington: Government Printing Office.

WASHINGTON, H.: **Manual of the Chemical Analysis of Rocks.** New York: Wiley, 8°, 200 pp., $2.00.

WOHL, PROF. A.: **Organische Chemie und die Lehre vom Leben.** Danzig: Schwital & Rohrbeck.

WOODWARD, C. J: **Five-figure Logarithms and Tables for Chemists.** New York: Spon & Chamberlain.

VOL. XXXII. OCTOBER, 1910. No. 10.

THE JOURNAL

OF THE

American Chemical Society

ANNUAL REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1911.

Received August 25, 1910.

In the autumn of 1909 the Council of the Chemical Society of London voted unanimously in favor of issuing the annual report of the International Committee on Atomic Weights in September or October instead of in January, as heretofore. In that proposition the Chemical Society of France has concurred, and American sentiment has also been favorable to the suggested change. Therefore the change is now made.

The reasons offered for the new policy are very simple: First, the school year, at least in most educational institutions, begins in the autumn. It is desirable that teachers should then have the latest table of atomic weights at their command, in order to avoid changes after school work has begun. Secondly, publishers of text-books are accustomed to issue their new works in the autumn, and often request early information as to changes which are likely to be made. The proposed change in the time of issuing the table is therefore an aid to teachers, students and publishers, and no disadvantage to any one else. The immediate usefulness of the table is increased, and to attain that end should be a main purpose of the committee.

Since the preparation of the report for 1910, a number of important memoirs upon atomic weights have appeared. The results obtained are, in brief, as follows:

Chlorine.—The density, composition by volume, and compressibility of hydrochloric acid have been measured by Gray and Burt[1] with great care. From the density and volumetric composition, when H = 1.00762, Cl = 35.459. From the density and compressibility, Cl = 35.461.

---

[1] *J. Chem. Soc.*, **95**, 1633.

The mean, 35.460, is the value given in the annual table of atomic weights for the past two or three years.

The density of hydrochloric acid has also been determined by Scheuer,[1] who gives measurements made under varying conditions. His final conclusion, based upon his own work after comparison with that of Gray and Burt, is that Cl = 35 466.

Lithium.—Richards and Willard,[2] in their important research upon the atomic weight of lithium, measured three distinct ratios; namely, silver to lithium chloride, silver chloride to lithium chloride, and lithium perchlorate to lithium chloride. From these ratios, without the intervention of any others, the following independent values for three atomic weights are obtained:

Li = 6.939
Cl = 35.454
Ag = 107.871

The value for silver varies from the accepted value, 107.88, by about one part in 12000, which is probably less than the actual uncertainty. That for chlorine diverges more widely, namely, by about one part in 6000. The new figures are undoubtedly entitled to great weight, but in view of the excellent work done by others it would be unwise to make any hasty change in the table. For lithium, however, the value 6 94 may be taken, replacing the old 7.00.

Strontium.—Thorpe and Francis,[3] in their determinations of the atomic weight of strontium, measured six ratios, and obtained the following results:

Ratio 2Ag to $SrBr_2$,	Sr = 87.645
Ratio 2AgBr to $SrBr_2$,	Sr = 87.653
Ratio 2Ag to $SrCl_2$,	Sr = 87.642
Ratio 2AgCl to $SrCl_2$,	Sr = 87.645
Ratio $SrBr_2$ to $SrSO_4$,	Sr = 87.629
Ratio $SrCl_2$ to $SrSO_4$,	Sr = 87.661
Mean of all,	Sr = 87.646

The value adopted by the authors is 87.65. Richards' figure is 87.62. An intermediate value, 87.63, is adopted in the new table.

Phosphorus.—Atomic weight redetermined by Baxter and Jones.[4] From the ratio between silver and silver triphosphate the authors find P = 31.043, when Ag = 107.88. The rounded-off figure 31.04 is to be adopted.

Vanadium.—From the ratio between silver chloride and vanadyl trichloride, Prandtl and Bleyer[1] find V = 50.963 and 51.133 in two series of experiments.

---

[1] *Z. physik. Chem.*, **68**, 575.

[2] THIS JOURNAL, **32**, 4.

[3] *Proc. Roy. Soc., London A*, **83**, 277.

[4] THIS JOURNAL, **32**, 298.

In a later paper, Prandtl and Bleyer,[2] also from analyses of vanadyl trichloride, find V = 51.061. From reductions of V_2O_5 to V_2O_3 they found V = 51.374. The latter method, however, they regard as uncertain. The value V = 51.06 may be provisionally adopted.

Tellurium.—Marckwald and Foizik,[3] by a somewhat complex volumetric process, based on the oxidation of TeO_2 by $KMnO_4$, conclude that Te = 127.61. This agrees with many of the other recent determinations of the constant, but is not sufficiently exact to supplant the value given in the table.

Rhodium.—Two inaugural dissertations upon the atomic weight of rhodium have been issued from Gutbier's laboratory at Erlangen. Renz reduced rhodium pentammine bromide in hydrogen and found Rh = 102.92. H. Dittmar,[4] by similar reductions of the corresponding chloride, found Rh = 102.93.

Platinum.—The very elaborate investigation of Archibald[5] upon the atomic weight of platinum was based upon analyses of the chloroplatinates and bromoplatinates of potassium and ammonium. In all, 28 ratios were measured, giving values for Pt ranging between 195.19 and 195.25. Their arithmetical mean gives Pt = 195.22. Archibald, however, in his final discussion, uses only 12 ratios, giving, in mean, Pt = 195.23. The figure 195.2 is given in the table.

The Inert Gases.—The densities and molecular weights of helium and neon have been redetermined by Watson.[6] For the atomic weights he finds He = 3.994 and Ne = 20.200. In another paper[7] he applies the critical constants of krypton and xenon to their densities as determined by Moore, and finds Kr = 82.92 and Xe = 130.22. There are also new determinations of the density of argon, by Fischer and Hahnel.[8] Their mean value, referred to O = 16, is 19.945, a figure rather higher than that given by Ramsay and Travers. It corresponds to an atomic weight of A = 39.89.

It is also to be noted that a third, revised, edition of Clarke's "Recalculation of the Atomic Weights" has recently been published by the Smithsonian Institution.

---

[1] *Z. anorg. Chem.*, 65, 152.

[2] *Ibid.*, 67, 257.

[3] *Ber.*, 43, 1710. See also Browning and Flint, *Am. J. Sci.*, [4] 28, 347, who adduce evidence to show that tellurium is possibly complex.

[4] Reproduced in *Sitz. phys. med. Soz. Erlangen*, 40, 184.

[5] *Proc. Roy. Soc. Edinburgh*, 29, 721.

[6] *J. Chem. Soc.*, 97, 810.

[7] *Ibid.*, 97, 833.

[8] *Ber.*, 43, 1435.

The annual table of atomic weights for 1911 follows, with but few changes from that of the preceding year.

International Atomic Weights, 1911.

	Symbol.	Atomic weight.		Symbol	Atomic weight.
Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.0	Osmium	Os	190.9
Boron	B	11.0	Oxygen	O	16.00
Bromine	Br	79.92	Palladium	Pd	106.7
Cadmium	Cd	112.40	Phosphorus	P	31.04
Caesium	Cs	132.81	Platinum	Pt	195.2
Calcium	Ca	40.09	Potassium	K	39.10
Carbon	C	12.00	Praseodymium	Pr	140.6
Cerium	Ce	140.25	Radium	Ra	226.4
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.5	Samarium	Sa	150.4
Copper	Cu	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.4	Silicon	Si	28.3
Europium	Eu	152.0	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gadolinium	Gd	157.3	Strontium	Sr	87.63
Gallium	Ga	69.9	Sulphur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.0
Glucinum	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	159.2
Helium	He	3.99	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.85	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.06
Lead	Pb	207.10	Xenon	Xe	130.2
Lithium	Li	6.94			
Lutecium	Lu	174.0	Ytterbium (Neoytterbium)	Yb	172.0
Magnesium	Mg	24.32	Yttrium	Yt	89.0
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.0	Zirconium	Zr	90.6

Signed, F. W. Clarke,
T. E. Thorpe,
W. Ostwald,
G. Urbain.

THE ATOMIC WEIGHT OF MERCURY.

(SECOND PAPER.)

BY C. W. EASLEY.

Received July 30, 1910.

In a series of experiments on the atomic weight of mercury, described in a previous communication,[1] mercuric chloride of very great purity was prepared and its analysis tended to show that the accepted value of this constant was too low. This conclusion was reached as a result of work having to do with the ratio $HgCl_2 : 2AgCl$. Since the results differ from the accepted value by three-tenths of one per cent., it seemed best to establish their correctness in a general way before publication. This was done by determining the percentage of mercury in mercuric chloride but it was explicitly stated that the method of verification was involved and did not approach in accuracy the one by which the ratio $HgCl_2 : 2AgCl$ was determined and that the former was employed merely to indicate the general neighborhood in which the true value lay. The value obtained by this, less accurate, method differed from the first by less than one-tenth of one per cent. but the process was so questionable from the standpoint of the complete collection[2] of the mercury that the same ratio has been determined in another way by work in this laboratory. The results corroborate and agree very closely with the higher value previously published. To determine this ratio, the metal was deposited electrolytically from mercuric chloride of the same degree of purity as that employed in the previous work, the methods of preparation being identical. The value obtained, 200.63, is in almost exact agreement with the finding of the previous investigation, 200.62, calculated from the ratio $HgCl_2 : 2AgCl$, which was believed to give a result with very small error.

Historical and Critical Survey.

In order to find a possible source of error in the work of previous investigators, it may be best to append the work already published.

The table brings to light the fact that mercury itself constitutes one term of every ratio. The metal has been liberated from the several compounds by two methods: (1) by heating with calcium oxide or copper in a stream of an inert gas by means of which the mercury was swept out of the tube containing the reacting mixture, the vapor being condensed in a portion of the apparatus used subsequently for weighing the deposit; (2) by depositing the metal on a platinum dish with the aid of the electric current. It is not unlikely that the first method is subject to loss of mercury through imperfect condensation, as it will be shown later that the vapor pressure of mercury at rather low temperatures, although small, is sufficient to be of considerable importance. This would seem to be the main point of weakness in all the previous work, as the preparation of the compounds in a fairly pure condition, with the exception of the oxide, appears to be a comparatively simple matter.[2] Whether any of the compounds escaped contact with the lime or copper, however, might be questioned. The process was certainly complete in the electrolytic method of Hardin but the details concerning such an important matter as the drying of the deposit are so meager that the results do not carry the weight that their agreement would otherwise warrant.

---

[1] THIS JOURNAL, 31, 1207.

[2] That a small portion of the finely divided metal passed by the filter in the process of its separation from the filtrate containing the chlorine was known from the solvent action of the mercury salt on the silver chloride. This was described in the previous paper. In fact, only a few of the attempts to collect and determine the mercury were successful, owing to its tendency, under the conditions of the experiments, to be precipitated in such a finely divided state.

	Ratio.	Atomic weight
Turner (*Phil. Trans*, 1833, 531)	$HgO : Hg$	200.63
Erdmann and Marchand (*J. prakt. Chem.*, 31, 395)	$HgO : Hg$	200.20
Hardin (THIS JOURNAL, 18, 1003)	$HgO : Hg$	200.04
Erdmann and Marchand (*J. prakt. Chem.*, 31, 395)	$HgS : Hg$	200.52
Turner (*Phil. Trans.*, 1833, 531)	$HgCl_2 : Hg$	199.67
Millon (*Ann. chim. phys.*, 18, 345)	"	200.22
Svanberg (*J. prakt. Chem.*, 45, 472)	"	199.71
Hardin, (THIS JOURNAL, 18, 1903)	"	200.06
" " " " "	$HgBr_2 : Hg$	199 80
" " " " "	$Hg(CN)_2 : Hg$	199.84
" " " " "	$Hg : Ag$	199.92
Turner[1] (*Phil. Trans.*, 1833, 531)	$HgCl_2 : 2AgCl$	.....

The loss of mercury at low temperatures due to its vapor pressure, however slight, is not to be overlooked. At a given temperature, the loss would obviously depend upon the rate at which the vapor was swept through the condensing tube, or, in the case of drying deposits on platinum dishes, on the amount of convection currents in the immediate neighborhood. In the first case, it is entirely possible that the condensation of the mercury, its partial pressure in the mixture being small, from the stream of hot gas was not complete in spite of the fact that gold leaf was employed to collect the portions which might escape. The question involved in the later electrolytic work is the same but here we have to do with the metal spread over the surface of a dish which "was washed several times with boiling water and carefully dried." The temperature and method of drying are not stated.

---

[1] In this determination, no account whatsoever was taken of the solvent action of mercury salts on silver chloride so that the values have been excluded from the table as being subject to known error. The results were abnormally high.

[2] It was shown in the previous paper that the sublimation of the chloride from material containing water, such as recrystallized salt, is attended with the production of a slight amount of basic salt.

It is well-nigh impossible to reproduce the exact conditions under which various observers have worked but some experiments were undertaken to show the effect of evaporation at moderately low temperatures on the weight of mercury. However, no attempts at exaggerating the ordinary drying methods were made. Instead of exposing a considerable surface of the metal such as a deposit on a dish, a globule of dry mercury having a surface of 1.5 sq. cm. was placed in a weighing bottle 3 sq. cm. in cross section and 5 cm. in height. The bottle was placed in an air oven and maintained for such periods of time and at such temperatures as are shown in the accompanying table. Under such conditions there are no air currents to any extent and no other liquid whose vaporization would tend to carry away the mercurial vapor with it.

Hours in oven.	Temperature of oven	Total loss in grams.	Loss in grams per hour.
3	50°	0.0016	0.00053
4½	50	0.0024	0.00053
10	50	0.0033	0.00033
6	50	0.0027	0.00048
3½	50	0.0010	0.00029
19	50	0.0057	0.00030
8	60	0.0050	0.00063

The results are as concordant as one might expect and even under these conditions, where the evaporation is reduced to a minimum, the loss is considerable. Especially in the case of a mercury deposit on a platinum dish,[1] the effect is not to be neglected because of the relatively large error[2] due to the small amount of mercury which may be satisfactorily dealt with in this manner.

In the following work, in view of the errors which might arise from the volatility of the metal, it was decided to dry the mercury at ordinary temperatures, using acetone to remove the water as was done in the previous work. The error committed by this procedure is exceedingly small although under favorable conditions the evaporation of mercury may be measured at quite low temperatures. Thus, in a room, subject to draughts, at a temperature of 25°, a slight though decided loss was noticed on several occasions when a considerable surface of mercury was exposed for 24 hours.

---

[1] The manuals on electro-analysis do not agree on the temperature at which mercury should be free from water. One commonly used, however, recommends the drying on a moderately warm plate.

[2] Thus, with one gram of mercuric chloride, the average amount used by Hardin, each change of a tenth of a milligram of the metal in the neighborbood of the actual amount present affects the atomic weight in the first decimal place.

General Method.

In order to secure recognition of the higher value of the atomic weight of mercury by any method, the latter must be free from the objections urged against the process used in determining the same ratio as described in the preliminary paper.[1] The electrodeposition of mercury from the chloride under proper conditions realizes this condition to a marked degree. That the metal is completely freed from the chlorine by this process is well known and its complete collection is assured from the form of the apparatus. Again, electrolytic methods in general possess simplicity. In the work here described even greater simplicity, and therefore greater accuracy, has been attained from the manner in which the deposit is handled. A special vessel was devised in which the metal was deposited in globular form by means of a mercury cathode and without being removed was washed by decantation, freed from water by means of acetone and finally weighed. A test of the method is whether a globule of mercury can be subjected to the above-mentioned treatment without change of weight. Many experiments bearing on this point show that the changes in weight, a similar vessel receiving similar treatment, of course, serving as a counterpoise, are small, never being greater than a tenth of a milligram and generally no more than a few hundredths. Such changes may therefore be attributed to errors incident to weighing glass vessels of the size employed. By the electrolysis of known weights of mercuric chloride with precautions to be mentioned later, one has a method at once simple and accurate and possessing the very great advantage, other things being equal, that relatively large amounts of mercury may be deposited without increasing the error of measurement. Over twenty grams of mercuric chloride were electrolyzed in the tube with the same ease and accuracy as were the smaller amounts.

The Material.—For the sake of comparison with the work previously published, three samples of mercuric chloride were prepared with the same care and in precisely the same manner as in that work. For the details reference should be made to that paper. The corresponding samples are designated by the same numbers in both communications. The analyses of these samples are considered in a series by themselves for the reason that no suspicion whatever is attached to the purity of either the salt or the mercury obtained from it.

Not so much can be claimed for sample o which was originally intended for the preliminary work in order that some uniformity of results might be attained while the method was being tested out. To this end, the choicest appearing crystals from Kahlbaum's highest grade of mercuric chloride were sublimed in a current of dry air in the special tube described in the previous paper. A large fraction coming over first was discarded, but most of the remainder was collected. During the sublimation, the temperature was maintained in the neighborhood of, 300°. An exceedingly small residue, for commercial material, remained, which had every appearance of being carbon. The salt was entirely soluble in water.

---

[1] This Journal, 31, 1207.

The results of the analyses of this sample were quite concordant, and a search was begun to discover the nature of the traces of impurities for it was evident that very pure salt was being dealt with. Slight amounts of arsenic only could be found in the original Kahlbaum salt and none whatever in the sublimed portion, so that it was decided to use the results of the analyses of this sample as evidence in this investigation. Naturally, less weight must be attached to the results from this sample, subjected to physical treatment only in its purification, than to the values from samples 1, 2, and 3, especially as the latter samples were the last to be analyzed and thus greater manipulative skill was possible at this stage of the work. That some impurity was present, however, was evidenced from the fact that the globule after drying had a peculiarly striated appearance here and there, although the surface was lustrous. Any metal deposited simultaneously must have been present in very small amounts and would probably have dissolved in the mercury. The deposition of platinum was not the cause for the same phenomenon did not occur with any of the other samples. Judging from the high results, if a foreign metal is present, it must have an atomic weight higher that that of mercury, which is quite improbable. The sample gives a result so little above that of the final series, however, that the difference might be accounted for by the retention of a minute quantity of water or even acetone by the peculiar surface which, in turn, might have been caused by the slightest amount of an impurity.[1]

Weighing.—A Sartorius balance was used and the consecutive weighings could be relied upon to one-fortieth of a milligram. In determining the weight of the salt, substitution was the method employed while, in the case of the mercury, the tube containing the metal was counterpoised with a similar tube and was subjected to the process of double weighing in order to correct for the inequalities in the length of the balance arms.

---

[1] That the presence of very small amounts of certain impurities interferes with the tendency of the separate particles to unite is well known. In washing the mercury obtained from this sample, the particles sometimes became detached and considerable more difficulty was experienced in reuniting them than in the case of the other samples. It is not impossible that a small amount of packing material, often found in chemicals, was destroyed during the sublimation and that some of the products distilled over so that the appearance of the mercury might be due to very small detached particles of the metal itself covered with a film of organic matter.

The gold-plated brass weights were calibrated and the proper corrections applied. The following vacuum corrections were made:

+0.000080 gram per gram of mercuric chloride.
—0.000055 gram per gram of mercury.

The Cathode.—In view of the difficulties attending washing and drying deposits on platinum dishes. it was decided very early in the course of the work to make use of a mercury cathode, an idea due to Wolcott Gibbs[1] in 1883 and used by him and others in depositing various metals in the form of amalgams. The main drawback to the more general adoption of such a method has been the difficulty of handling the deposit, an objection which has been overcome in this work. In the present case, such a cathode seems ideal in that it avoids an interface of any considerable area with another conducting surface, with the consequent questionable procedure of washing and drying under such circumstances. Again, one is not limited to the deposition of very small amounts of metal, which amounts cannot be exceeded in using platinum dishes, owing to the tendency of the mercury to collect in drops at the bottom of the dish; nor does the question of current density arise to change the nature of the deposit.

To discover whether or not hydrogen was retained by the mercury, a dilute solution of hydrochloric acid in one case and of sulphuric acid in another was electrolyzed and the effect on the weight of the cathode was determined. In one of the experiments only was there an increase in weight, so that the change in this exceptional case was considered accidental. Had this effect been caused by hydrogen, the atomic weight of mercury would have been changed only one unit in the second decimal place.

For the electrode, five to ten grams of mercury, prepared by the reduction of pure mercuric chloride, was placed in the electrolyzing tube in contact with the platinum wire. The mercury was first washed with water, treated with acetone and dried with air, as will be described later. At the conclusion of some of the experiments, a portion of the deposited metal was retained to serve as a cathode, thereby effecting a saving in the preparation of pure mercury. The globule constituting the cathode always possessed a clean, lustrous surface.

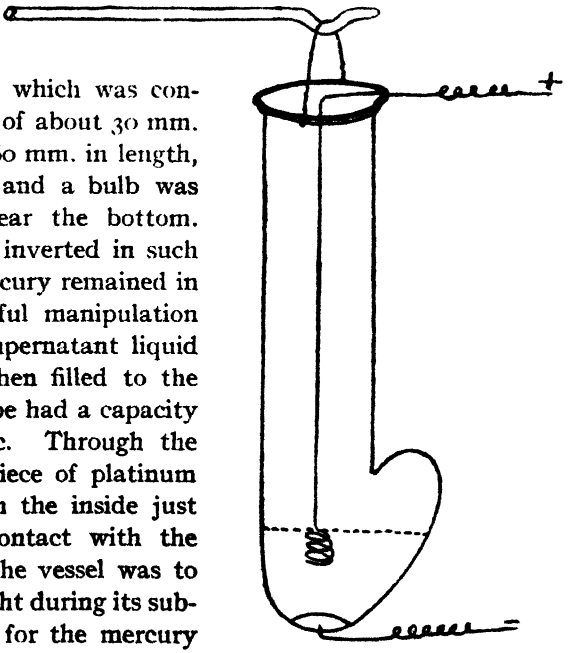
The Anode.—As concentrated solutions of mercuric chloride were to be electrolyzed with the consequent production of strong chlorine solutions, considerable time was spent in search for suitable anode material, for it was expected that platinum would be strongly attacked. Carbon in several of its forms was tried but it was not to be relied upon, either because of its absorptive properties or because of the tendency of portions to become detached. Again, such electrodes are difficult to treat in such a manner that constant weight is maintained and thus one has no check on this important point. In describing a method of overcoming the solvent effect of chlorine on a rotating platinum anode, Smith[1] recommends the use of a layer of toluene or xylene on the solution just above the anode. This was tested, although in this work the anode was stationary, with the result, as afterward found, that more of the platinum was dissolved by this treatment than without the absorptive layer. It was therefore decided to use the platinum, as is ordinarily done, find its loss of weight, determine the amount in the solution after the electrolysis and thus calculate by difference the amount deposited with the mercury. Contrary to expectations, the loss of platinum by solution was exceedingly small and practically all of the dissolved portion was deposited with the mercury, none being found in solution at the conclusion of an experiment. The anode at the beginning of the experiments described later weighed 1.54895 grams and at their conclusion 1.54880; or, during the course of eleven experiments in which over 125 grams of mercuric chloride had been electrolyzed, the anode lost 0.00015 gram.

---

[1] *Am. Chem. J.*, 13, 571.

The platinum wire, weighing 1.5 grams and having a length of 35 cm., was wound at one end into a spiral, the latter being maintained at approximately 2 cm. from the cathode. The other end of the wire was connected with the battery terminal by means of a clip.

The Electrolyzing Tube.—The figure illustrates the essential features of this vessel, which was constructed of glass tubing of about 30 mm. diameter. The tube, 160 mm. in length, was closed at one end and a bulb was blown into its side near the bottom. The tube could thus be inverted in such a manner that the mercury remained in the bulb and by careful manipulation practically all of the supernatant liquid could be removed. When filled to the top of the bulb, the tube had a capacity of approximately 50 cc. Through the bottom was sealed a piece of platinum wire which projected on the inside just far enough to make contact with the mercury cathode. As the vessel was to remain unaltered in weight during its subsequent treatment, save for the mercury



---

[1] *Electroanalysis.*

deposited, all portions of the surface were carefully smoothed in the flame. To this same end, the platinum wire was connected with the battery terminal by means of a clip which precluded any abrasion of the surface of the platinum. For convenience during the processes of electrolysis and weighing, a platinum wire was wound about the neck of the tube to serve as a loop for suspension. During the former process, the tube hung on a glass rod; in weighing, the hooks on the balance arms were utilized as supports. It has already been stated that a counterpoise, similar in every respect to the electrolyzing tube, was used throughout the work. Consecutive weighings proved the adequacy of this procedure.

The Procedure.—A known amount of mercuric chloride[1] was placed on the cathode in the electrolyzing tube with sufficient water to make a total volume of 25 or 30 cc., the sides of the tube having been carefully washed down. A few drops of a dilute solution of redistilled hydrochloric acid were added to make the solution approximately one-fortieth normal. This was necessary to increase the conductivity of the solution at the outset and this particular compound was chosen in order not to introduce ions other than those which would be present later. The water added was not sufficient to entirely dissolve the salt so that the latter was dissolved, except in so far as its solubility was affected by the presence of substances formed during the course of the process, only as the solution became depleted by the electrolysis. With the strength of current used, the action had ordinarily proceeded for 8 or 10 hours before the disappearance of the solid phase. At the end of a similar period, the action was complete, as shown by the preliminary work, but traces of mercury compounds were probably adhering to the sides of the tube and to the funnel placed in the mouth of the tube to prevent loss in the form of spray. An addition of approximately 20 cc. of water was made in washing the funnel and walls of the tube and the current was allowed to pass several hours longer, after which no trace of mercury could be detected in the solution. Sometimes the whole process consumed 48 hours, varying altogether with the amount of salt to be electrolyzed and whether or not it was convenient to perform the subsequent operations. Copious fumes of chlorine escaped during the action and as is usual in the electrolysis of mercuric chloride, insoluble particles said to be the mercurous compound gradually accumulated at the anode only to fall off and finally disappear. To prevent any of these particles from becoming permanently lodged between the glass surface and the cathode, the globule was agitated by a gentle whirling motion of the tube. This was not attempted, however, until the electrolysis was practically complete for fear of entangling solution and from that time on the process was repeated at intervals to insure completeness. At no time was the agitation violent enough to sever the connection between the mercury and platinum Sometimes the mercury exhibited a tendency to assume a form perhaps "deadened" and the separate particles had no tendency to unite with the main globule. Gentle tapping, however, generally sufficed to cause the formation of one globule.[1] It is not unlikely that the disengagement of hydrogen from the cathode was the cause of the separation of these small particles.

---

[1] The non-hygroscopic character of the salt was proven in the previous work.

To free the tube of conducting material at the end of the electrolysis, a funnel, with its stem almost reaching to the surface of the mercury, was placed in the tube and without breaking the electric connections at least 500 cc. of pure water were poured into the tube, the overflow being caught in a large porcelain dish where any particles of escaping mercury could be detected. During the washing process, the tube was rotated as previously described so that no chlorine would be retained between the cathode and glass and thus remain in contact with the mercury after the breaking of the circuit. After removing the funnel, the water in the tube was decanted, the mercury with perhaps a drop or so of water remaining in the tube, owing to the bulb arrangement. Five washings were made with redistilled acetone, each being decanted in turn. The tube was next immersed to its neck in a bath of acetone to free the outer surface of water and was finally hung on a glass rod to dry. The counterpoise was subjected to exactly the same treatment. The two tubes hung side by side and were gently agitated from time to time to prevent the possibility of the retention of any acetone between the globule and glass. Meanwhile, a current of air of the same intensity was passed over each globule so that in a short time the vapor of acetone was effectually removed and the tubes were full of air ready for their transfer to the bal-

THE RESULTS.

PRELIMINARY EXPERIMENTS

No. of expt	Sample of $HgCl_2$.	Weight of $HgCl_2$ in vacuum	Weight of Hg in vacuum	Atomic weight[2] of mercury.
1...........	0	10 05743	7.43123	200.68
2...........	0	8.41289	6.21687	200 71
3[3]..........	0	10.99056	8.11897	200.52
4...........	0	10.28282	7 59681	200.58
5...........	0	19.57120	14.46032	200.65
			Mean,	200.63

---

[1] In the preliminary experiments where less pure mercuric chloride was being dealt with, more difficulty was encountered.

[2] Calculated on the assumption that chlorine has the value, 35.46, THIS JOURNAL, 32, 4.

[3] In expt. 3, a portion of the mercury became detached and during the washing was poured into the catch dish. It is possible that the low value obtained in this case may be explained by the incomplete recovery of the separated particles.

ance arms. As soon as constant temperature was attained, the weighing was made by the method described before. Repetition of the drying process insured its completeness.

The current was supplied by three storage cells and was reduced by means of a suitable resistance to one- or two-tenths of an ampere. The action proceeded quietly, no spray being noticeable and no rise of temperature above 30° took place.

FINAL EXPERIMENTS.

No. of expt.	Sample of $HgCl_2$.	Weight of $HgCl_2$ in vacuum.	Weight of Hg in vacuum	Per cent Hg in $HgCl_2$.	Atomic weight[1] of mercury.
1.........	2	8.14695	6.01909	73.882	200.61
2.........	1	11.03881	8.15592	73.884	200.64
3	1	13.48192	9.96129	73.886	200.66
4..	3	11.08026	8.18610	73.880	200.60
5.........	3	11.31231	8.35819	73.886	200.66
6.........	3	21.44026	15.84060	73.882	200.62
				73.883	200.63

It now remains to consider the results in this and in the previous paper:

Series		Atomic weight.
1.	The ratio $HgCl_2$: Hg (from the previous paper)....	200.48
2.	" " $HgCl_2$: 2AgCl (from the previous paper).	200.62
3.	" " $HgCl_2$: Hg (prelim. expts, this paper)..	200.63
4.	" " $HgCl_2$: Hg (final " " ")...............	200.63

Giving each series equal weight, the mean value of the atomic weight of mercury becomes 200.59. It is reasonable, however, in seeking an optimum result to reject any series known to be faulty either on account of the nature of the material dealt with or in method. For the last reason, Series 1 is dropped and for the first, Series 3 is thrown out. Considerable weight is attached to the mean value, 200.63, of the two remaining series for (1) the mercuric chloride analyzed was the same in each, and, from the manner of preparation, it must have been practically free from foreign material and (2) the complete analysis, by methods which seem above question and which are radically different, shows that the sum of the mercury and chlorine contents gives essentially the real value. Thus,

Per cent. Mercury:

From the fact that 56.52119 g. of mercury resulted from 76.50051 g. of mercuric chloride (Series 4)........................ 73.883

Per cent. Chlorine:

On the basis that 86.21813 g. of silver were obtained from 81.66510 g. of mercuric chloride (Series 2)........................ 26.118

The sum...... .... 100.001

THE UNIVERSITY OF MAINE.

---

[1] In the calculations, the atomic weight of chlorine has been taken as 35.46, THIS JOURNAL, 32, 4.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE ATOMIC WEIGHT OF TANTALUM.[1]

BY CLARENCE W. BALKE.

Received July 1, 1910.

Introduction.

Of the previous determinations of the atomic weight of this element, those by Berzelius,[2] Rose,[3] Hermann[4] and Blomstrand[5] need not be considered, as their material was too impure to give results of value. The determinations of Marignac,[6] which appeared in 1866, were far more satisfactory. He analyzed potassium fluotantalate, K_2TaF_7, and the corresponding ammonium salt, $(NH_4)_2TaT_7$. In the case of the potassium salt he obtained the following percentages:

Ta_2O_5, 56.50, 56.75, 56.55, 56.56; K_2SO_4, 44.37, 44.35, 44.22, 44.24.

The ammonium salt gave the following percentages of tantalum oxide: 63.08, 63.24, 63.27, 63.42. These numbers were corrected for a small amount of potassium sulphate which was present in the oxide, due to the fact that he was unable to prepare the ammonium fluotantalate free from traces of the potassium salt.

If in the calculations the atomic weights of the elements involved are taken as given in the 1910 International Table the following values for the atomic weight of tantalum are obtained:

From the ratio, $K_2TaF_7 : Ta_2O_5$	182.4 to 184.6
From the ratio, $K_2TaF_7 : K_2SO_4$	181.6 to 182.9
From the ratio, $K_2SO_4 : Ta_2O_5$	181.9 to 183.0
From the ratio, $(NH_4)_2TaF_7 : Ta_2O_5$	180.5 to 183.8

It will be observed that there is a variation of several whole units between the individual determinations, yet for about forty years the accepted value of this constant was based on these results.

In 1906 Hinrichsen and Sahlborn[7] published a series of determinations in which metallic tantalum was burned to the oxide. The method has great simplicity, but it appears very doubtful to the writer if this metal can be prepared sufficiently pure for the purposes of atomic weight work. Their results follow on page 1128.

Here again there is a variation of over one unit between the individual determinations. Clarke,[8] after reviewing these various determinations of the value of this constant, remarks that its uncertainty probably amounts to as much as a unit.

---

[1] Presented at the San Francisco meeting of the American Chemical Society.

[2] *Pogg. Ann.*, 4, 14 (1825).

[3] *Ibid.*, 99, 80 (1856).

[4] *J. prakt. Chem.*, 70, 193 (1857).

[5] *Acta Univ. Lund*, 1864.

[6] *Arch. sci. phys. nat.*, (2) 26, 89 (1866); also *J. prakt. Chem.*, 99, 23.

[7] *Ber.*, 39, 2600 (1906).

[8] A Recalculation of the Atomic Weights, *Smithsonian Miscellaneous Collections*, Vol. 54, No. 3 (1910).

Wt. of Ta.	Wt. of Ta_2O_5.	Per cent. O.	At. wt. Ta.
0.37200	0.45437	22.12	180.65
0.41278	0.50364	22.01	181.77
0.33558	0.40975	22.10	180.98
0.35883	0.43807	22.08	181.14
0.47554	0.58087	22.15	180.59
			Mean, 181.03

While carrying out an investigation on columbium[1] it was found possible to make a satisfactory determination of the atomic weight of that element through the conversion of its pentachloride into the corresponding oxide. Consequently the writer decided to carry out a similar investigation with tantalum chloride, and, in general, the methods used were very similar to those employed in the former work.

Preparation of Materials.

In the preparation of all materials used during the investigation great care was exercised in the cleaning of all containing vessels and especial care was taken to exclude dust. Whenever possible the apparatus used was made continuous by fusing the various parts together, and this was always the case where chlorine was being used. In the case of chemicals not especially purified, those of the highest purity obtainable were employed.

Chlorine.—The chlorine used, including that used in the preparation of the sulphur monochloride, was made by allowing hydrochloric acid to drip upon potassium permanganate contained in a large flask. The acid used was prepared by distilling the constant boiling mixture from large Jena retorts. During the first part of the distillation small quantities of potassium permanganate were added from time to time and the first portions of the distillate were rejected. The chlorine was passed through a wash bottle containing water, two containing sulphuric acid and finally through a tower one meter long containing glass pearls and so arranged that the latter could be moistened from time to time with concentrated sulphuric acid.

Sulphur Monochloride.—This compound was prepared by passing a stream of chlorine over molten sulphur which had been crystallized previously from carbon disulphide. The apparatus was so constructed that the liquid could be redistilled from the receiver without transferring the material. The first portions of the distillate were rejected and the final product was collected directly in sealing flasks through which a stream of dry, filtered air had been allowed to flow.

Nitric Acid.—The nitric acid used in the determinations was distilled twice from a platinum retort, the middle third of the distillate being retained in each case. The acid was preserved in quartz flasks.

---

[1] Balke and Smith, THIS JOURNAL, 30, 1637 (1908).

Water.—The water used, including that employed in the final recrystallizations of the potassium fluotantalate, was prepared by redistilling the ordinary distilled water of the laboratory, after the addition of alkaline permanganate, from a still ordinarily used in the preparation of conductivity water.

Tantalum Chloride.—This compound was prepared by the ignition of tantalum oxide in a current of chlorine and the vapors of sulphur monochloride. The oxide used for preparations I and II was prepared from some of the potassium fluotantalate which had been obtained by Hall and Smith[1] from the columbite of South Dakota, and which was very kindly furnished me by Professor Edgar F. Smith.[2] This salt was recrystallized four times from water containing appreciable amounts of redistilled hydrofluoric acid, and only the first crops of crystals were used in the next crystallization. These operations were carried out in platinum and hard rubber dishes and hard rubber funnels were used in the filtration of the solutions. The final crop of crystals was heated in platinum dishes with concentrated sulphuric acid, which had been distilled from platinum, until most of the acid had been expelled. The residue was washed by decantation with large amounts of pure water. After this washing was complete, the mass was strongly ignited in platinum or quartz crucibles. Tantalum oxide prepared in this way has been shown to be pure.[3]

The oxide used for the third preparation of the chloride was obtained from the columbite of South Dakota as follows: The finely ground mineral was fused with potassium hydroxide in large iron crucibles; the mass was dissolved in water and the solution, after filtration, was treated with sulphuric acid, which precipitated the metallic acids. These were washed with water by decantation and then dissolved in an excess of hydrofluoric acid. The addition of potassium hydroxide to this solution gave a precipitate of potassium fluotantalate.[4] The final purifications were carried out as previously outlined.

The apparatus used for the preparation of the chloride is shown in Fig. I. The tantalum oxide (50–100 grams) was introduced into the hard Jena glass tube H, the ends of which were connected with the bulbs E and I by means of carefully ground joints which were lubricated with a trace of graphite. These joints were wrapped with several thicknesses of asbestos paper and the bulb of a thermometer was inserted in the latter at G and the temperature regulated so as to prevent a deposition of the chloride at this point. A stream of chlorine was passed through the apparatus by means of the tube B for 3–4 hours, the entire apparatus being heated with a free flame in order to remove any traces of moisture which might be present. At this time the tube H containing the oxide was heated to a low red heat for the same purpose. Sulphur monochloride was then run into the bulb E through C and heated to boiling. The oxide was slowly converted directly into the chloride which together with the excess of sulphur monochloride collected in bulb I. When all of the oxide had been converted into chloride, leaving practically no residue in the tube H, the sulphur monochloride was driven on through the entire apparatus and collected in O. The tantalum chloride was then distilled over into the bulb J and the apparatus sealed off at L. The two-way stopcock was then turned so as to deliver chlorine through D. The tantalum chloride was heated to boiling and the entire apparatus heated, so that the residue of sulphur monochloride and some of the tantalum chloride was driven over into O. The entire amount of chloride was then distilled over into K and finally into the small bulbs N. The chloride in all the bulbs was then brought to the boiling point and a small amount distilled over into the receiver O to insure the re-

---

[1] This Journal, 27, 1369 (1905).

[2] The author wishes to take this opportunity to express his appreciation for this and many other kindnesses shown him by Professor Smith.

[3] Balke, This Journal, 27, 1140.

[4] My thanks are due to one of my students, Mr. Lloyd Almy, who carried out this preliminary work.

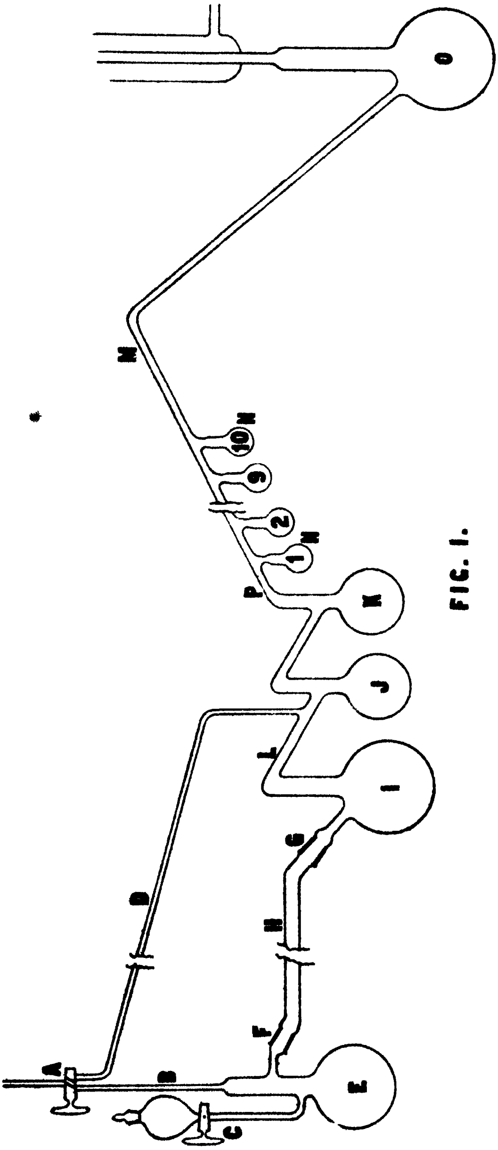


FIG. 1.

moval of the last traces of sulphur monochloride. When cold the apparatus was sealed off at P and M and finally the individual bulbs were sealed off. These contained from 5–20 grams of chloride.

The tantalum chloride so prepared was absolutely white in color, having none of the pale yellow tint which this compound is usually said to possess. When fused the chloride had a pale straw-yellow color. Five grams of this chloride were thrown into a flask containing bromine water, and the contents heated for several hours. The tantalum hydroxide was filtered out and the filtrate was evaporated to a very small bulk. This remained perfectly clear after the addition of a solution of barium chloride, which was taken to indicate that no sulphur remained in the preparation.

Density of Tantalum Chloride.—The density of this chloride was determined in carbon tetrachloride and the number 3.62 obtained. Tantalum chloride is somewhat soluble in carbon tetrachloride, and consequently a more satisfactory determination was obtained when heptane was used. This liquid did not react with the chloride nor did any of the latter dissolve. The following results were obtained:

Wt. of Pycnometer	10 2313
Wt. of Pycnometer + $TaCl_5$	23.6545
Wt. of Pycnometer + H_2O	35.2073
Wt. of Pycnometer + heptane	28 4050
Wt of Pycnometer + heptane + $TaCl_5$	39.1710

t = 27° Density of $TaCl_5$ = 3.68

Density of Tantalum Oxide.—As was found in the case of columbium oxide, the density of the tantalum oxide obtained from the present determinations varied quite appreciably, the numbers 8.62, 7.91, and 8.06 having been obtained. The density of this substance is not far from that of the weights used which were taken as having a density of 8.4 and it was found unnecessary to make a vacuum correction in the case of this substance.

Analyses of Tantalum Chloride.

The ratio studied was that of tantalum chloride to tantalum oxide, the transformation being made in quartz bulbs provided with tightly ground stoppers of quartz or glass. One of Ruprecht's best balances was used in the work and the weights were carefully standardized. All weighings were made by substitution, using a tare of the same material and very nearly the same weight as the object being weighed. The excess weight of the quartz bulb and its stopper over the tare was determined. By carefully tapping one of the small bulbs containing the tantalum chloride the latter was broken up into small pieces and by means of a file and a hot rod a crack was drawn about two-thirds of the way around the neck of the bulb. This bulb, together with the weighed quartz bulb, into the neck of which had been slipped a wide-neck funnel tube, were introduced into a gas-tight box supplied with a removable plate-glass top. Two holes had been cut in the sides of the box and rubber gloves were attached on the inside. This box contained a large amount of calcium chloride, and a stream of air, which had been passed through large amounts of sulphuric acid and then filtered through glass wool, was passed through the apparatus for several hours. By slipping the hands into the gloves it was possible to remove the top of the bulb containing the chloride and introduce the latter into the quartz bulb without soiling the neck of the bulb. In this way it was possible to effect the only transfer of material involved in the determinations in an atmosphere of dry air. After replacing the stopper in the quartz bulb the latter was removed from the box and the excess of weight over the tare again determined. The bulb was next placed in a vacuum desiccator containing water and the air pumped out. In one or two days the chloride had completely hydrolyzed and the greater part of the hydrochloric acid produced had dissolved in the water outside of the bulb. A small amount of water and a few cc. of concentrated nitric acid were introduced into the bulb and the mass evaporated to dryness with the aid of the apparatus shown in Fig. II. The hood B was fastened to the neck of the bulb by means of the split rubber stopper E, which was prevented from actual contact with the neck of the bulb by means of a strip of filter paper. F was a double-walled steam bath. D contained cotton to filter the air which was drawn slowly through the apparatus by means of a water pump attached at C. The mass was evaporated to dryness three times, a little water and a small amount of nitric acid being added each time. This insured the removal of the hydrochloric acid before the final ignition, which was made with a good blast lamp arranged so that both the air and gas were filtered through cotton in order to mini-

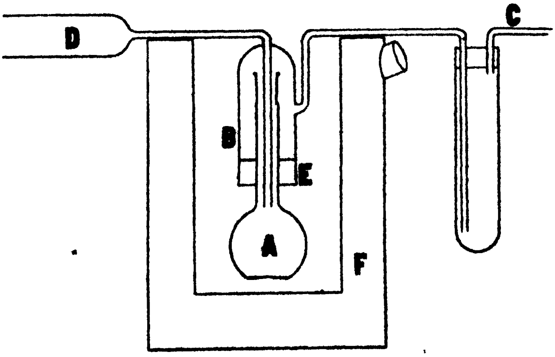


FIG. II.

mize the amount of dust which might be blown against and adhere to the sides of the bulb. These ignitions were continued until no further loss of weight was observed. In making the calculations the atomic weight of chlorine was assumed to be 35.46. The temperature of the balance and the barometric reading were recorded in the case of the individual weights and these numbers were used in applying the vacuum corrections. In the calculation the density of tantalum chloride was taken as 3.68 and that of the weights as 8.4. As mentioned previously, no vacuum correction was applied in the case of the tantalum oxide, since this correction, which was smaller than the error in weighing, affected the fifth decimal only. The following table includes the results of all determinations made which were carried to completion without accident.

Series	Bulb.	Wt of $TaCl_5$ (vac.).	Wt. of Ta_2O_5 (vac).	100 parts of $TaCl_5$ — parts of Ta_2O_5	At wt. of Ta
II	3	12.99680	8.02326	61 733	181.49
II	5	9.24957	5.71104	61 744	181.60
II	4	10.17456	6.28133	61.736	181.52
II	1	17.99542	11.11014	61.739	181.55
II	2	11.70558	7.22693	61.739	181.55
III	4	6 24767	3.85658	61.728	181.46
III	3	7.26375	4.48398	61.731	181.48
I	2	15.88270	9.80465	61 732	181 49
					Mean, 181.52

Summary.

In eight experiments 91.51605 grams of tantalum chloride gave 56.49791 grams of tantalum oxide, corresponding in round numbers to 181.5 as the atomic weight of tantalum, a number one-half a unit higher than that now given in the international table. In conclusion, it may be as well to state that further work upon the value of this constant is in progress.

URBANA, ILL.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 57.]

THE IONIZATION RELATIONS OF SULPHURIC ACID.

BY A. A. NOYES AND M. A. STEWART.

Received July 22, 1910.

CONTENTS.

INTRODUCTION.—OUTLINE OF THE INVESTIGATION AND REVIEW OF PREVIOUS WORK.
PART I.—SOLUTIONS OF SULPHURIC ACID.
1. The Hydrogen-Ion Concentration Derived from Freezing-Point Measurements.
2. The Hydrogen-Ion Concentration Derived from Conductance and Transference Measurements.
3. The Equivalent Conductance of Hydrosulphate Ion Derived from Conductance and Transference Measurements.

4. The Hydrogen-Ion Concentration Derived from Catalysis Experiments.
5. The Hydrogen-Ion Concentration Derived from the Relative Effects of Sulphuric and Hydrochloric Acids upon the Ionization of Picric Acid.
6. Comparison of the Hydrogen-Ion Concentrations Derived by Various Methods.
7. Concentration of the Other Constituents.
8. Relative Concentrations of Un-ionized Sulphuric Acid Derived from Distribution Experiments.

PART II.—SOLUTIONS OF SODIUM HYDROGEN SULPHATE.

9. Transference Measurements.
10. Summary of the Transference Results.
11. Conductance Measurements.
12. Concentrations of the Sodium Ion and Hydrogen Ion Derived from the Transference and Conductance Data.
13. The Hydrogen-Ion Concentration Derived from Catalysis Experiments.
14. Concentrations of the Other Constituents.

SUMMARY.

INTRODUCTION.—OUTLINE OF THE INVESTIGATION AND REVIEW OF PREVIOUS WORK.

It is commonly assumed that sulphuric acid in aqueous solution ionizes in two stages according to the reactions

$$H_2SO_4 = H^+ + HSO_4^- \quad \text{and} \quad HSO_4^- = H^+ + SO_4^{=},$$

but no investigation, except that of Noyes and Eastman,[1] which was begun after this one, has furnished valuable evidence as to the proportion of the intermediate hydrosulphate ion (HSO_4^-) present, or indeed as to its existence in the solution. This research was therefore undertaken with the hope of furnishing more definite knowledge in regard to the ionization relations of this important acid.

The separate determination of the ionization constants for the two hydrogens is attended with much greater difficulty in the case of this acid than in the case of almost any of the organic dibasic acids or of such inorganic acids as sulphurous or phosphoric acid. This is true for the reasons, first, that the first hydrogen, and probably also the second hydrogen, of sulphuric acid is so largely ionized that the mass-action law cannot be employed in the study of its equilibrium relations; and second, that the difference between the degrees of ionization of the two hydrogens of sulphuric acid is much smaller than in the case of the other acids referred to, thus causing both stages of its ionization to be superposed, and preventing, among other things, a direct determination of the conductance of the intermediate hydrosulphate ion, a knowledge of which is of great importance in interpreting the conductance and transference data. In consequence of these difficulties many of the commonly applied methods fail to give, in this case, reliable results.

Thus it might be thought that the transference experiments which have previously been made by several investigators would throw much light upon the question of the intermediate ion; but the following simple calculation shows that the transference number would not be greatly different whether the acid be completely ionized in the one way or the other, provided a certain probable value be assumed for the conductance of the hydrosulphate ion. The number of chemical equivalents of sulphate ion transferred for each faraday of electricity passed would evidently be given in the two cases by the expressions:

---

[1] *Carnegie Institution Publications*, 63, 239–81 (1907).

$$\frac{\Lambda_{SO_4}}{\Lambda_H + \Lambda_{SO_4}} \text{ and } \frac{2\Lambda_{HSO_4}}{\Lambda_H + \Lambda_{HSO_4}}$$

respectively, where the Λ's represent the equivalent conductances of the ions indicated by the subscripts. At 18° the value of the first expression is $68/(68 + 315) = 0.178$; and, assuming that hydrosulphate ion has the same conductance as acetate ion,[1] the value of the second expression would be $70/(315 + 35) = 0.200$, provided in both cases it be assumed that Λ_H has the value (315) which it has at zero concentration. The matter is, however, complicated by the uncertainty as to the value of Λ_H that should be used in calculating the transference number at higher concentrations. Thus, if we put $\Lambda_H = 330$ in accordance with the transference results of Noyes and Sammet and of Noyes and Kato[2] with 0.006–0.018 normal acids, the transference number for complete ionization into hydrogen ion and sulphate ion becomes 0.171, and for that into hydrogen ion and hydrosulphate ion becomes 0.192. Experimentally the transference number for sulphuric acid at 18° in 0.01 to 0.05 formal[3] solution has been found by Tower and by Jahn and Hugbrechts to be 0.176, within a limit of error that can hardly exceed 0.002. These considerations indicate that a not very large proportion of hydrosulphate ion is present; but they also show that, on account of the errors involved in the measurement and interpretation of the transference number, it does not furnish a satisfactory means of calculating the concentration of that ion. It will be shown below, however, that the transference data do furnish valuable evidence as to the equivalent conductance of the hydrosulphate ion, and that, assuming that ion is really present in considerable proportion, they confirm the approximate validity of Noyes and Eastman's assumption in regard to it.

The existing freezing-point determinations, made by a great number of different investigators,[4] show that hydrosulphate ion is at 0° largely dissociated. Thus, in 0.05 formal solution, the value of the mol number i (representing the mols from one formula weight) has been found to be about 2.22, while in 0.01 formal solution values between 2.42 and 2.56 have been obtained. Complete ionization into H^+ and HSO_4^- would, of course, require the value 2.00, and into $2H^+$ and $SO_4^{=}$ the value 3.00. Moreover, it will be shown below that the quantity $(i - 1)$ is equal to the number of equivalents of hydrogen ion resulting from one formula weight of sulphuric acid (that is, $i - 1 = C_H/C$, where C is the formal concentration of the sulphuric acid), and that therefore freezing-point values furnish a quantitative measure of the concentration of this constituent.

---

[1] This assumption was made in all their computations by Noyes and Eastman, but without other basis than the apparently similar molecular complexity of the two ions.

[2] See *Carnegie Institution Publications*, 63, 326 (1907).

[3] In accordance with the practice now followed in this laboratory, the term "formal" is here used to express a solution containing one formula weight (in this case of H_2SO_4) per liter of solution.

[4] For references see the following section.

The experiments on the relative catalytic influences of sulphuric acid and of hydrochloric acid upon the rate of hydrolysis of cane sugar and of ethyl acetate also furnish a means of determining the proportion of hydrogen ion in sulphuric acid solutions. The results will be considered more fully below. It may be mentioned here, however, that those of Ostwald on the sugar inversion indicate that at 25° in 0.05 formal solution 1.20 equivalents of hydrogen ion result from one formula weight of sulphuric acid; and that those of Kay on the ethyl acetate catalysis indicate that at 35° at the same concentration 1.16 equivalents result.

Noyes and Eastman,[1] upon the basis of certain probable assumptions, have derived from their conductance measurements with sulphuric acid and potassium hydrogen sulphate through a wide range of temperature definite estimates of the concentrations of sulphate ion and of hydrosulphate ion in solutions of both of these substances. Thus they estimate that in a 0.05 formal solution of sulphuric acid at 18° there are 6 per cent. H_2SO_4, 61 per cent. of HSO_4^-, and 33 per cent. of $SO_4^{=}$. This corresponds to 127 per cent. of hydrogen ion, which is in rough agreement with the results of the hydrolysis experiments just referred to. In view of the assumptions involved in their estimates, independent determinations of the concentrations of these constituents seem very desirable.

From the existing thermochemical data on the heat of neutralization of sulphuric acid, Noyes and Eastman have also calculated the heat of ionization of the hydrosulphate ion, and have found that it corresponds roughly with the heat value derived from the change of dissociation of that ion with the temperature.

The purpose of this article is to discuss critically the existing data relating to sulphuric acid and the conclusions to be drawn from them, and to present the results of some new work, which includes measurements of the conductance of sulphuric acid and sodium hydrogen sulphate, transference experiments with solutions of this salt, experiments upon the relative effect of sulphuric and hydrochloric acids upon the ionization of picric acid, and determinations of the distribution of sulphuric acid between water and amyl alcohol.

---

[1] *Carnegie Institution Publications*, 63, 274–6 (1907).

PART I.—SOLUTIONS OF SULPHURIC ACID.

1. The Hydrogen-Ion Concentration Derived from Freezing-Point Measurements.

The equivalents of hydrogen ion resulting from one formula weight of the acid can be calculated from the value of the mol number i, as determined from the freezing-point lowering, by merely subtracting unity from it; that is, $C_H/C = i - 1$. For evidently:

$$iC = C_H + C_{H_2SO_4} + C_{HSO_4} + C_{SO_4}, \text{ and } C = C_{H_2SO_4} + C_{HSO_4} + C_{SO_4},$$

where C represents the formal concentration of the acid and the C's with subscripts the formal concentration of the constituents represented by those subscripts.

The freezing points of dilute sulphuric acid solutions have been determined by Pickering,[1] Loomis,[2] Jones,[3] Wildermann,[4] Ponsot,[5] Barnes,[6] Hausrath[7] and Bedford.[8] In order to determine the best values at a series of round concentrations and to form an estimate of their probable accuracy, the results of all these investigators (except the early ones of Pickering) have been correlated and combined by a method described by Noyes and Falk.[9] Only the values of $i - 1$ or C_H/C corresponding to the final values of i derived by them need therefore be reproduced here. It seems scarcely possible that any of these values at the concentrations 0.02 to 0.1 formal inclusive are in error by as much as 2 per cent., but those at 0.01 and 0.005 may well be in error by two or three times this amount.

TABLE I.—VALUES OF THE HYDROGEN-ION CONCENTRATION (C_H/C) AT 0° DERIVED FROM FREEZING-POINT MEASUREMENTS.

Formal concentration	0.005	0.010	0.020	0.025	0.050	0.100
C_H/C	1.59	1.47	1.35	1.32	1.22	1.13

2. The Hydrogen-Ion Concentration Derived from Conductance and Transference Measurements.

Noyes and Eastman, as stated in the introduction to this article, derived from their conductance measurements alone, with the aid of certain assumptions, an estimate of the hydrogen-ion concentration in sulphuric acid solutions at various concentrations and temperatures. Making the assumption that the HSO_4^- ion has the same equivalent conductance as the acetate ion, they first showed that the hydrogen-ion concentration must lie between certain comparatively narrow limits. Then making the further assumption, based on the conductivity results at high temperatures, that sulphuric acid has with respect to its first hydrogen the same ionization tendency as hydrochloric acid, definite values of the concentrations of all the constituents in the solution were derived.

---

[1] *J. Chem. Soc.*, 57, 363 (1890). See also *Z. physik. Chem.*, 7, 397 (1891).

[2] *Physic. Rev.*, 1, 281 (1893).

[3] *Z. physik. Chem.*, 12, 629 (1893).

[4] *Ibid.*, 15, 350 (1894); 19, 241 (1896).

[5] *Ann. chim. phys.*, [7] 10, 109 (1897).

[6] *Trans. Royal Soc. Canada*, [2] 6, III, 48 (1900). See also *Trans. N. S. Inst. of Science*, 10, 222 (1900).

[7] *Drude's Ann.*, 9, 547 (1902).

[8] *Proc. Roy. Soc., London A* 83, 454 (1910).

[9] THIS JOURNAL, 32, 1027 (1910).

It may readily be shown that the first and most arbitrary of these two assumptions can be dispensed with by combining with the conductance values the results of transference experiments. Thus for the specific conductance L we have

$$1000\ L = C_H\Lambda_H + 2C_{SO_4}\Lambda_{SO_4} + C_{HSO_4}\Lambda_{HSO_4}, \qquad (1)$$

where the C's represent the formal concentrations and the Λ's the equivalent conductances of the various ions. And for the number of equivalents (N_{SO_4}) of SO_4 transferred per faraday of electricity, we have

$$N_{SO_4} = \frac{2C_{SO_4}A_{SO_4}}{1000\ L} + \frac{2C_{HSO_4}A_{HSO_4}}{1000\ L}. \qquad (2)$$

This follows from the principle that the quantity in equivalents of each ion transferred per faraday is equal to the ratio of its conductance to the whole conductance and from the fact that one electrical equivalent of HSO_4 ion yields two chemical or analytical equivalents of SO_4. Writing this equation in the form

$$\tfrac{1}{2} \times 1000\ L\ N_{SO_4} = C_{SO_4}A_{SO_4} + C_{HSO_4}A_{HSO_4}, \qquad (3)$$

subtracting it from equation (1), dividing both members by C, the formal concentration of the sulphuric acid, and putting $1000L/2C = A$, the equivalent conductance of the acid, we get

$$2A\,(1 - \tfrac{1}{2}N_{SO_4}) = \frac{C_HA_H}{C} + \frac{C_{SO_4}A_{SO_4}}{C}. \qquad (4)$$

The last term of this expression is relatively small and can vary only between the limits zero and $\frac{1}{2}(C_H/C)A_{SO_4}$, corresponding to the two limiting cases where HSO_4^-, and where $SO_4^{=}$, is the only anion present. Within corresponding limits the value of C_H/C can therefore be determined, and evidently without involving any assumption as to the value of A_{HSO_4}.

Let us now consider the transference and conductance data available for this calculation.

The transference number for sulphuric acid has been determined by many different investigators,[1] but only the determinations by Bein, by

---

[1] Wiedmann, *Pogg. Ann.*, 99, 162 (1856); Hittorf, *Ibid.*, 106, 401 (1859); Bein, *Z. physik. Chem.*, 27, 52 (1898); Starck, *Ibid.*, 29, 394 (1899); Tower, THIS JOURNAL, 26,

Tower, and by Jahn and Hugbrechts, seem to have been made with precautions sufficient to warrant the consideration of the results. The following table contains the final values obtained by them for the transference number of the anion (N_{SO_4}) reduced to uniform temperatures by means of the temperature coefficient 0.0011[1], and in the case of Jahn and Hugbrecht's results interpolated for round concentrations.

TABLE II.—TRANSFERENCE NUMBER FOR THE SULPHATE ION.

Formal concen	At 8°		At 20°		At 32°.		At 97°.
	Bein	Tower.	Tower.	J & H.	Tower	J. & H.	Bein.
0.5000	..	...	0.188	...	...	...	...
0.250		.	0.187	..	..	...	...
0.125			...	0.170	...	...	...
0.100		.	0.181	...	...	...	...
0.050	.	0.164	0.176	0.177	0.192	..	..
0.025	0.172	0.164	0.179	0.177	0.192	0.194	0.304
0.010		0.168	0.181	0.178	0.191	0.189	..
0.004		..	.	0.158		0.164	..

From these results one is justified in concluding that the transference number is substantially constant between 0.01 and 0.05 formal, and that within this concentration interval it has the following values:

0°.	8°.	18°	20°	25°.	32°.
0.157[2]	0.165	0.176	0.178	0.184	0.192

At the higher concentrations 0.1 to 0.5 formal Tower's data are to be regarded as the best values, in view of the concordance of his results with the cathode and anode portions, and of the constancy in content of the middle portions.

Two entirely independent series of measurements of the conductance of sulphuric acid at 25° have recently been made in this laboratory, by Mr. G. W. Eastman[3] and by Mr. F. L. Hunt,[4] respectively, and a series at 0° with the same solutions has been made by the latter.[5] The

---

1062 (1904); Jahn and Hugbrechts, *Z. physik. Chem.*, **58**, 651 (1907); Whetham and Paine, *Proc. Royal Soc.*, A**81**, 69 (1908).

[1] This is the value found by Tower for the temperature-coefficient ($\Delta N_{SO_4}/\Delta T$) between 8 and 32° for 0.01 to 0.05 formal solutions. The reduction was in no case for a greater interval than 3°.

[2] This value is extrapolated, but can in consequence hardly be in error by more than 0.001.

[3] *Carnegie Institution Publications*, **63**, 262 (1907).

[4] In connection with a research which is soon to be published in detail.

[5] Measurements with dilute sulphuric acid have been previously published at 18° by Kohlrausch (L.-B.-M. Tabellen, p. 746); at 0 and 18° by Barnes (*Proc. Royal Soc. Canada*, [2] **6**, III, 46 (1900)); at 0, 15, 25 and 35° by Jones and Douglas (*Am. Chem. J.*, **26**, 436 (1901)); see also Tower's "Conductivity of Liquids," p. 164); at 0 and 18° by Whetham (*Z. physik. Chem.*, **33**, 351 (1900); **55**, 205 (1906)); and at 18° to 306° by Noyes and Eastman (*Loc. cit.*).

results of these determinations are presented in the following table. The concentrations are expressed in formula weights per liter at the temperature of the measurement, and the equivalent conductance in reciprocal ohms:

TABLE III.—EQUIVALENT CONDUCTANCE OF SULPHURIC ACID AT 25° AND 0°.

Formal concn.	25°. N. & E.	25° F. L. H.	25°. Mean.	0°. F. L. H.
0.1000	...	234.7	234.7	165.4
0.0500	251.2	251.2	251.2	177.2
0.0250	273.0	273.1	273.0	191.5
0.0125	...	299.3	299.2	206.9
0.00625	327.5	...	327.5	...
0.00500	(337.0)	336.8	336.8	226.4
0.00100	390.8	...	390.8	...
0.00025	413.7	...	413.7	..
0.00010	418.5	. .	418.5	..

Besides the transference and conductance data for the acid, the values of the equivalent conductances of hydrogen ion (Λ_H) and sulphate ion (Λ_{SO_4}) are needed for the computation of C_H/C. For Λ_H at zero concentration, Goodwin and Haskell[1] and also Kohlrausch[2] have derived the value 315 at 18°, which corresponds to 348 at 25° if the temperature coefficient ($d\Lambda/\Lambda_{18}dT = 0.0153$) given by Kohlrausch be employed. For Λ_{SO_4} the value given by Kohlrausch[2] at 18° is 68, which, using his temperature coefficient (0.0227), becomes 79 at 25°.

The values of Λ_H and Λ_{SO_4} at 0° at zero concentration we have found to be 224 and 43, respectively, by the following method of derivation. Noyes and Coolidge,[3] from their measurements at 0° of the conductance of potassium chloride (which are perfectly concordant with those of Whetham), obtained the value 81.4 for Λ_0 for that salt. Multiplying this by the transference number 0.496 (assumed to be the same as at 18°) we get $\Lambda_K = 40.3$ and $\Lambda_{Cl} = 41.1$. Furthermore, Λ_0 for HCl at 0° was found to be 265.4 by multiplying Λ_0 for HCl at 18° = 379.5 by the ratio of the Λ values for 0.01 normal HCl at 0° and 18°, which ratio has been found to be 0.700 by Barnes[4] and 0.6994 by Déguisne.[5] Subtracting $\Lambda_{Cl} = 41.1$, we then obtain $\Lambda_H = 224$.[6] Similarly, Λ_0 for K_2SO_4 at 0° was found to be 83.1 by multiplying Λ_0 for K_2SO_4 at 18° = 132.6 by the ratio of the Λ values for 0.001 normal K_2SO_4 at 0° and at 18°, which ratio has the value 0.627 (0.628 according to Archibald[1] and 0.625 according to Déguisne). Subtracting $\Lambda_K = 40.3$, we get $\Lambda_{SO_4} = 42.8$.

---

[1] *Phys. Rev.*, 19, 395 (1904).

[2] *Z. Elektrochem.*, 13, 333 (1907).

[3] *Carnegie Institution Publications*, 63, 47 (1907).

[4] *Trans. N. S. Inst. of Science*, 10, 150 (1900).

[5] See *Landolt-Bornstein-Meyerhoffer Tabellen*, p. 755.

[6] Attention may here be called to the fact that Johnston's rough estimate of Λ_H at 0° as 240 (THIS JOURNAL, 31, 1015 (1909)) is much too high.

It should be mentioned, however, that the transference experiments of Noyes and Sammet[2] and of Noyes and Kato[3] with hydrochloric and nitric acids have indicated that the equivalent conductance of hydrogen ion is about 5 per cent. greater in 0.005 to 0.02 normal solutions of these acids than it is at zero concentration. It seems reasonable to assume that this may be also the case in sulphuric acid solutions; and it seems therefore worth while to show in the subsequent calculations the effect of this assumption, according to which Λ_H would have the value 365 at 25° and 235 at 0°. At the same time it should be recognized that the employment of these particular values at higher concentrations than 0.02 normal has at present no experimental basis.

The values of C_H/C at 25° and at 0°, calculated from the foregoing data by means of equation (4) under the two limiting assumptions that C_{SO_4} is equal to zero and to $\frac{1}{2}C_H$, respectively, and for the two values of Λ_H just referred to, are given in the following table The first values given in each column are those corresponding to the assumption that SO_4 is the only anion present:

TABLE IV VALUES OF C_H/C AT 25° AND 0° DERIVED FROM CONDUCTANCE AND TRANSFERENCE MEASUREMENTS.

Formal concen	C_H/C at 25° (for $\Lambda_H = 348$)	C_H/C at 25° (for $\Lambda_H = 365$)	C_H/C at 0° (for $\Lambda_H = 235$)	C_H/C at 0° (for $\Lambda_H = 224$).
0.100	1.10–1.22	1.05–1.16	1.19–1.29	1.24–1.36
0.050	1.18–1.31	1.13–1.24	1.27–1.39	1.33–1.46
0.025	1.28–1.42	1.23–1.35	1.38–1.49	1.44–1.57
0.0125	1.40–1.56	1.34–1.48	1.48–1.61	1.55–1.70
0.00625	1.53–1.71	1.46–1.62	....	......
0.00500	1.58–1.76	1.51–1.67	1.63–1.77	1.70–1.86

3. The Equivalent Conductance of Hydrosulphate Ion Derived from Conductance and Transference Measurements.

The value of the equivalent conductance of the hydrosulphate ion is of so much importance in the interpretation of transference and conductance results that it is worth while to consider just what conclusion in regard to it can be drawn from the existing data. For this purpose we may make use of equation (3), written in the form:

$$\Lambda N_{SO_4} = \Lambda_{SO_4}(C_{SO_4}/C) + \Lambda_{HSO_4}(C_{HSO_4}/C). \qquad (5)$$

In this equation N_{SO_4}, Λ, and Λ_{SO_4} are known; and between C_{SO_4}, C_{HSO_4}, and C_H (which last is known within comparatively narrow limits) there exists the following relation expressing the equality of the equivalent concentrations of the positive and negative ions:

---

[1] *Trans. N. S. Inst. of Science*, 10, 38 (1898).

[2] THIS JOURNAL, 24, 958 (1902).

[3] *Ibid.*, 30, 333 (1908).

$$C_H = 2C_{SO_4} + C_{HSO_4}. \qquad (6)$$

In order that Λ_{HSO_4} might be definitely determined by these equations, either C_{SO_4} or C_{HSO_4} would have to be known; but it is found by computation that the value involved is such that it can be determined within narrow limits, provided only the assumption is justified that the concentration C_{HSO_4} forms a reasonably large part (say as much as one-fourth) of the total ion concentration $(C_{HSO_4} + 2C_{SO_4})$. Thus the values of Λ_{HSO_4} calculated by (5) from the data given in Tables II, III and IV under the limiting assumption that $C_{HSO_4} = C$ and under the assumption that $C_{HSO_4} = \frac{1}{4}C_A$, and with the values of C_H/C corresponding to the smaller and larger values of Λ_H are given in Table V.

TABLE V.—CALCULATED VALUES OF THE EQUIVALENT CONDUCTANCE OF HYDROSULPHATE ION AT 25° AND 0°

Concentration.	At 25°.				At 0°.			
	For $C_{HSO_4} = C$		For $C_{HSO_4} = \frac{1}{4}C_H$.		For $C_{HSO_4} = C$.		For $C_{HSO_4} = C$	
	$\Lambda_H = 348$	$\Lambda_H = 365$.	$\Lambda_H = 348$.	$\Lambda_H = 365$	$\Lambda_H = 224$	$\Lambda_H = 235$	$\Lambda_H = 224$	$\Lambda_H = 235$
0.100	36.0	38.4	37.0	44.0	18.9	20.2	13.8	17.6
0.050	35.1	37.5	34.0	41.0	18.8	20.1	14.1	17.6
0.025	35.3	37.7	34.5	41.0	18.8	20.2	14.5	18.3
0.0125	35.3	37.7	34.5	42.0	18.8	20.5	15.1	19.1
Mean,	35.4	37.8	35.0	42.0	18.8	20.2	14.4	18.1

It is evident from these calculations that at 25° the value of Λ_{HSO_4} is 35 ± 1 if $\Lambda_H = 348$, or 40 ± 2 if $\Lambda_H = 365$, and that at 0° the value is 16 ± 2 if $\Lambda_H = 224$, or 19 ± 1 if $\Lambda_H = 235$, it being always assumed that the HSO_4^- ion is present in sufficient proportion to make the calculated values significant. It will be noted that the value 40 at 25° or 19 at 0° for Λ_{HSO_4} is not far from one-half of that for Λ_{SO_4} (79 or 43), which would be the case if the frictional resistance to the motions of the two ions were nearly equal, since the electric force acting on the latter, owing to its double charge, is twice as great.

4. The Hydrogen-Ion Concentration Derived from Catalysis Experiments.

Since the catalytic influence of acids upon reactions of hydrolysis is nearly proportional to their hydrogen-ion concentration and is little influenced by other factors, the concentration of that ion in sulphuric acid solutions may be determined by comparing the effect of that acid on the reaction rate with that of an acid of known ionization, such as hydrochloric acid, at nearly the same ion concentration. The data that seem best adapted to this purpose are those of Ostwald[1] upon the sugar inversion and of Kay[2] on the ethyl acetate hydrolysis. Table VI contains the specific reaction rates as determined by these two investigators.

---

[1] Ostwald, *J. prakt. Chem.*, [2] 31, 313–4 (1885).

[2] Kay, *Proc. Royal Soc. Edinburgh*, 22, 493–496 (1898–9).

TABLE VI.—RELATIVE CATALYTIC EFFECTS OF SULPHURIC AND HYDROCHLORIC ACIDS.

Acid.	Formal concen	Sugar inversion at 25°.	Ethyl acetate hydrolysis at 35°.
HCl	0.5	20.5	...
	0.2	....	146.9
	0.1	3.34	71.8
	0.01	0.313	...
H_2SO_4	0.25	10.7	201.5
	0.05	2.08	44.1
	0.005	0.265	6.06

The best method of computation clearly seems to be to determine by interpolation the concentration (C_A) of a hydrochloric acid solution which has the same catalytic effect as each of the measured sulphuric acid solutions. This we have done (for the two most dilute solutions of the latter acid) by calculating first for the former acid the values of the ratio (k_A/C_A) of the specific reaction rate to the concentration, which values do not vary greatly with the dilution, interpolating for a concentration which is estimated to be nearly isohydric with the sulphuric acid solution in question, and then dividing the reaction rate for the latter acid by this ratio, the interpolation and division being once more repeated, if necessary. The concentration C_A of hydrochloric acid so obtained, when multiplied by the corresponding ionization (γ_A) as given by the conductance ratio (Λ/Λ_0), yields the hydrogen-ion concentration C_H in the solution of either acid, and this, when divided by the concentration of the sulphuric acid C_B, gives the mols of hydrogen ion resulting from one formula weight.

Two sets of values of the ionization γ_A were employed, these being obtained by dividing the values of Λ for hydrochloric acid at 18° found by Kohlrausch, Goodwin and Haskell, and Noyes and Cooper[1] in one case by $\Lambda_0 = 380$, and in the other case by $\Lambda_0 = 396$, corresponding respectively to the values of Λ_H at zero concentration (315), and at higher concentrations (331), as found by Noyes, Sammet, and Kato.

The data and results are given in Table VII:

TABLE VII.—VALUES OF HYDROGEN-ION CONCENTRATION AT 25° AND 35° DERIVED FROM CATALYSIS EXPERIMENTS.

C_B.	C_A at 25° (Ostwald)	C_A at 35° (Kay).	γ_A.	C_H/C_B, 25° (Ostwald).	C_H/C_B, 35° (Kay).
0.0500	0.0638	0.0619	0.940 or 0.902	1.20 or 1.15	1.16 or 1.11
0.0050	0.00847	0.00862	0.974 or 0.935	1.65 or 1.58	1.68 or 1.61

5. The Hydrogen-Ion Concentration Derived from the Relative Effects of Sulphuric and Hydrochloric Acids upon the Ionization of Picric Acid.

Experiments by M. A. STEWART.

A method which naturally suggests itself for the determination of the hydrogen-ion concentration is that based on the principle of isohydric solutions, which consists in finding the concentration which a solution of sulphuric acid must have in order that it may be mixed with a definite solution of hydrochloric acid with the production of a mixture whose specific conductance is the mean of that of the separate solutions. Theoretically this result occurs only when the hydrogen-ion concentrations of the two acids are equal. Both calculation and experiment clearly showed, however, that the sensitiveness of the method was so slight as to make it of no value.

---

[1] *Carnegie Institution Publications*, 63, 138 (1907).

A new method was therefore employed. This consists in principle in determining the relative concentrations of hydrochloric acid and of sulphuric acid which drive back the ionization of a third acid to the same extent. Picric acid was chosen as the third acid, and the condition of equal concentration of its un-ionized part in the solution was determined by shaking it with benzene, between which and water it distributes itself, as shown by the investigation of Rothmund and Drucker.[1]

The experiments were carried out in detail as follows: In one of two bottles of two-liter capacity were placed about 1300 cc. of the sulphuric acid solution to be investigated, and in the other the same volume of a hydrochloric acid solution (of a concentration estimated to be about isohydric); then to both were added an equal volume (about 70 cc.) of a nearly saturated solution of picric acid in benzene. These were rotated for four to five hours in a thermostat at 25°. The same volume (about 50 cc.) of the benzene phase was then removed from each, and, after the addition of a little water, each portion was titrated with about 0.3 normal barium hydroxide, using phenolphthalein as indicator. Then the experiment was repeated with a second solution of hydrochloric acid of somewhat different concentration from that first used, and the rate of change was computed of the concentration of the acid with the quantity of picric acid contained in the benzene phase,

$$\left(\frac{\Delta C_{HCl}}{C_{HCl}} \Big/ \frac{\Delta C_{HP}}{C_{HP}}\right);$$

and therefrom, under the assumption of proportionality, the concentration of hydrochloric acid which would have an effect just identical with that of the sulphuric acid was calculated.

The picric acid used was purified by crystallization from dilute hydrochloric acid, from benzene, from alcohol, and from water. The benzene used was the thiophene-free commercial product.

Preliminary experiments showed that no appreciable amount of either sulphuric acid or hydrochloric acid would go into the benzene. Normal sulphuric acid was shaken with 50 cc. of benzene; the benzene layer was separated, and to it were added a little water and phenolphthalein and then 0.1 normal alkali. One drop of the alkali gave as strong a coloration as in the case of pure water to which phenolphthalein was added, showing that no appreciable amount of sulphuric acid could have gone into the benzene. A similar experiment with normal hydrochloric acid gave the same result.

---

[1] *Z. physik. Chem.*, 46, 827–53 (1903).

The error due to the effect of the picric acid on the ionization of the sulphuric and hydrochloric acids is very small: first, because the amount of picric acid is relatively small, so that the hydrogen ion from it forms only a small part of the total hydrogen ion, and second, because the sulphuric and hydrochloric acids would be affected to nearly the same extent and in the same direction. Moreover, since the ion concentrations in the two acid solutions are nearly the same, an appreciable error can hardly arise through a variation in the distribution ratio for the picric acid between the two phases.

The experimental results, all of which are at 25°, are given in the following table. The fourth column shows the percentage difference in the concentrations of the picric acid in the two benzene solutions which had been shaken with the hydrochloric acid and with the sulphuric acid solutions. The values in heavy type in the rows below each group of experiments, show in the second and third columns the calculated concentrations of the two acids at which they have the same hydrogen-ion concen-

TABLE VIII. VALUES OF HYDROGEN ION CONCENTRATION AT 25° DERIVED FROM EXPERIMENTS WITH PICRIC ACID

Expt No.	Formal concentration C of H_2SO_4	Formal concentration of HCl	Percentage difference in picric acid concentrations	Percentage ionization of HCl	Hydrogen ion concentration C_H.	Ratio C_H/C.
1	0.4923	0.5547	−0.33	....	....	....
2	0.4923	0.5652	+0.03	....	....	....
	0.4923	**0.5645**	**±0.00**	**85.5**	**0.4826**	**0.98**
3	0.2500	0.3129	+2.59	....	....	....
4	0.2500	0.2535	−3.27	....	....	....
5	0.2500	0.3192	+2.99	....	....	....
6	0.2500	0.2825	−0.20	....	....	....
	0.2500	**0.2846**	**±0.00**	**88.8**	**0.2526**	**1.01**
7	0.09983	0.12022	+1.27	....	....	....
8	0.09983	0.11690	−0.23	....	....	....
	0.09983	**0.1174**	**±0.00**	**92.0**	**0.1080**	**1.08**
9	0.05000	0.05942	−1.19	....	....	....
10	0.05000	0.06089	−0.05	....	....	....
	0.05000	**0.06095**	**±0.00**	**94.1**	**0.0573**	**1.15**[1]
11	0.02506	0.03197	−0.42	....	....	....
12	0.02506	0.03253	−0.07	....	....	....
	0.02506	**0.03264**	**±0.00**	**95.8**	**0.03126**	**1.25**[2]

[1] Or 1.10, assuming $\Lambda_0 = 396$ and $100\gamma = 90.3$.

[2] Or 1.20, assuming $\Lambda_0 = 396$ and $100\gamma = 92.0$.

tration, and in the last three columns the corresponding values of the percentage ionization of the hydrochloric acid (as derived from its conductance ratio Λ/Λ_0, using Kohlrausch's data[1] at 18° and taking $\Lambda_0 = 380$), of the hydrogen-ion concentration C_H in either solution, and of the ratio C_H/C of that concentration to the formal concentration of the sulphuric acid. The calculated values of C_H and C_H/C would be 4 per cent. smaller than those gven in the table if in calculating the ionization Λ_0 be taken equal to 396. This may be justifiable for the two most dilute solutions, but any value assumed for the more concentrated solutions would be entirely arbitrary.

6. Comparison of the Hydrogen Ion Concentrations Derived by Various Methods.

The values of the hydrogen-ion concentration (C_H/C) derived by the methods already considered are brought together in Table IX. Excepting those derived from the freezing point, the values given are those calculated under the assumption that the equivalent conductance of hydrogen ion Λ_H is that derived from the conductance of acids at zero concentration. If it be assumed, in correspondence with the transference results of Noyes, Sammet, and Kato, that in acid solutions of medium concentrations Λ_H is 5 per cent. greater than at zero concentration, then all the values of C_H/C (except those derived from the freezing point) should be increased by 4 to 5 per cent.

TABLE IX.—VALUES OF THE HYDROGEN ION CONCENTRATION DERIVED BY VARIOUS METHODS.

Formal concentration.	Freezing point. 0°.	Conductance and transference.		Sugar catalysis. 25°.	Picric acid expts. 25	Ester catalysis 35°.
		0°.	25°.			
0.050	1.22	1.33–1.46	1.18–1.31	1.20	1.15	1.16
0.025	1.32	1.44–1.57	1.28–1.42	....	1.25	....
0.005	1.59	1.64–1.79	1.58–1.76	1.65	....	1.68

It will be seen that at 0° the values derived from the freezing points are much less than even the lower limiting values derived from the conductivity and transference experiments, which values were obtained under the assumption that only H^+ and $SO_4^=$ ions exist in the solution. This discordance may well be due in part to error in the value of (Λ_H) employed, but it can not be wholly accounted for in this way.

It will also be noted that the conductance and transference data show that there is a large decrease in the hydrogen-ion concentration between 0° and 25°. It will also be observed that the values derived from the conductance are in accordance with those derived from the sugar catalysis; but that they are considerably higher at 0.05 and 0.025 formal than those derived by the picric acid method. It may be recalled that a change in the assumed value of Λ_H will not account for this divergence, since it would affect the latter values to nearly the same extent as those from the conductance.

---

[1] As given in *Landolt-Börnstein-Meyerhoffer's Tabellen*, p. 746.

7. Concentration of the Other Constituents.

Since the values of the hydrogen-ion concentration calculated from the conductance and transference data differ by about 10 per cent. in the two limiting cases, in one of which no hydrosulphate ion and the other of which no sulphate ion is assumed to be present, it might seem that the proportion of these two ions in the solution might be obtained by considering in connection with these limiting values that of the hydrogen-ion concentration derived by some of the other methods. The degree of inaccuracy of all the values is, however, great enough to make such a calculation of little, if any, value. Indeed, the values obtained by the picric acid distribution methods (like those at 0° obtained from the freezing point) are below the lower limit of those derived from the conductance, so that upon solving the appropriate equations mathematically a negative value of the hydrosulphate ion concentration results.

In order to determine the concentration of the other constituents (SO_4^{--}, HSO_4^-, and H_2SO_4), further information in regard to at least one of them is therefore essential. The others would then become determined in virtue of the condition equations,

$$C_H + C_{HSO_4} + 2C_{H_2SO_4} = 2C, \tag{7}$$

and

$$C_{SO_4} + C_{HSO_4} + C_{H_2SO_4} = C. \tag{8}$$

To find a method which will give such information in a conclusive way is difficult. The most promising line of attack would seem to be to determine the concentration of the sulphate ion through the measurement of some property closely related to it; and in the hope of doing this we have studied the effects of sodium sulphate, sodium hydrogen sulphate, and sulphuric acid on the solubility of thallous sulphate. But the results of these experiments, which will be described in another article, show, even in the case of sodium sulphate, such a wide divergence from the law of the solubility product that it seems impracticable to employ them for the purpose in question. Another method, simpler in principle, of determining the sulphate-ion concentration in sulphuric acid solutions is to measure the electromotive force of a concentration cell, such as is represented by the combination Hg, Hg_2SO_4, K_2SO_4Aq, H_2SO_4Aq, Hg_2SO_4, Hg. Experiments of this kind are to be undertaken in this laboratory.

In the absence of information as to the sulphate ion the conclusion of Noyes and Eastman that the ionization tendency of sulphuric acid with reference to its first hydrogen is the same as that of hydrochloric acid is the only principle that seems to be sufficiently well substantiated to warrant being made the basis of a provisional computation of the constitution of sulphuric acid solutions.

That conclusion, it may be recalled, was based: (1) on the fact that at the temperature of 156° the formal conductance of potassium hydrogen sulphate (435) in 0.1 formal solution has become even less than that of potassium chloride (490), showing that the former salt can dissociate to an important extent only into K^+ and HSO_4^-, that therefore the ion HSO_4^- is only very slightly dissociated; (2) on the conclusion that this ion must *a fortiori* be very slightly dissociated in fairly concentrated solutions of sulphuric acid itself at 156° and above; (3) on the fact that the conductance of such solutions when interpreted under this assumption shows that the ionization of the acid is substantially equal to that of hydrochloric acid of the same concentration at 156, 218, and 306°; and (4) on the assumption that this equality of ionization holds true also at lower temperatures, such as 18°, inasmuch as differences in ionization of largely ionized substances are as a rule less pronounced at lower than at higher temperatures.

Upon the basis of this conclusion in regard to the un-ionized H_2SO_4, the concentration of the constituents may be calculated by equations (7) and (8) by using separately each of the values of C_H/C, given in Table IX. It has seemed worth while, however, to make such calculations only with the values at 0° derived from the freezing point and with the mean of the values at 25° derived from the sugar catalysis experiments and the picric acid experiments. We have, in addition, calculated the concentrations of the various constituents by the method described by Noyes and Eastman[1] from the conductance and transference data at 0° and 25°, so that the results may be compared on the one hand with those at 0° obtained from the freezing-point data, and on the other hand with those at 25° obtained by the catalysis and picric acid experiments. The results are given in Table X.

TABLE X.—CONCENTRATIONS OF THE CONSTITUENTS IN SULPHURIC ACID SOLUTIONS.

Formal concen.	C_H/C.	$C_{H_2SO_4}/C$.	C_{HSO_4}/C.	C_{SO_4}/C.	C_H/C.	$C_{H_2SO_4}/C$.	C_{HSO_4}/C.	C_{SO_4}/C.
	From conductance data at 0°.				From freezing-point data at 0°.			
0.050	1.38	0.06	0.50	0.44	1.22	0.06	0.66	0.28
0.025	1.48	0.05	0.42	0.53	1.32	0.05	0.58	0.37
0 005	1.67	0.02	0.29	0.69	1.59	0.02	0.37	0.61
	From conductance data at 25°.				From isohydric data at 25°.			
0.050	1.25	0.06	0.63	0.31	1.17	0.06	0.71	0.23
0.025	1.33	0.05	0.57	0.38	1.25	0.05	0.65	0.30
0.005	1.62	0.02	0.34	0.64	1.65	0.02	0.31	0.67

---

[1] *Loc. cit.*, p. 273.

8. Relative Concentrations of Un-ionized Sulphuric Acid Derived from Distribution Experiments.

Experiments by M. A. STEWART.

In the hope of furnishing further evidence as to the proportion of unionized H_2SO_4 in the sulphuric acid solutions, an attempt was made to find an organic solvent between which and water the acid would distribute itself to an appreciable extent. In this way at least the relative concentrations of H_2SO_4 in different solutions might be determined. Though the experiments made in this direction do not lead to very definite conclusions, yet they seem worthy of record.

Amyl alcohol was the only solvent that was found to take up from water a considerable quantity of sulphuric acid, and the commercial product did this in much less degree after it had been thoroughly washed with cold dilute sulphuric acid (one volume of the concentrated acid and two of water), with alkali, and with water, and distilled. It was, however, the so purified alcohol that was used for the following experiments.

The methods of measurement and of computation were as follows: The sulphuric acid solutions and amyl alcohol were shaken from four to six hours at 25°, in bottles which had previously been well steamed out in an inverted position and then quickly dried by a current of air. After settling clear, a certain volume of the alcohol phase was removed and shaken in a dry bottle with a certain volume of water which had been saturated with amyl alcohol at 25°. This second water phase was then separated and its specific conductance measured. The specific conductances of the first water phase (*i. e.*, the sulphuric acid solutions after they were shaken with the amyl alcohol) were also measured. The concentration of sulphuric acid in the first water phase and also its concentration in the amyl alcohol phase (derived from its concentration in the water with which that phase was shaken) were obtained from a plot of the cube root of the specific conductance against the ratio of the specific conductance to the concentration (L/C).

This method of determining the concentration of the sulphuric acid in the amyl alcohol was used because the concentrations were so small that by ordinary chemical methods of determination large errors would be likely to be introduced. The concentration of sulphuric acid in the first water phase had to be determined after the shaking because some of the water went into the amyl alcohol and some amyl alcohol went into it, thereby changing its concentration. The specific conductance of ordinary solutions of the acid in water could not be used in this case, for it was found that the amyl alcohol which went into the water phase decreased its specific conductance. Three experiments, made to determine the magnitude of the necessary correction, showed that the decrease of specific conductance due to saturation with amyl alcohol was

5 per cent. at 0.1897 formal, 7.2 per cent. at 0.0471 formal, and 7.6 per cent. at 0.0059 formal.

The specific conductance of a 0.0016 normal solution of sulphuric acid in amyl alcohol (obtained by shaking amyl alcohol with 0.094 normal aqueous sulphuric acid) was found to be less than 9×10^{-6}, which showed that the ionization of the sulphuric acid in the amyl alcohol was negligible.

The following tables contain the results. Under C_W is given the formal concentration of the sulphuric acid present after shaking in the aqueous phase, and under C_A/C_W the ratio to this concentration of that (C_A) in the amyl alcohol phase. An *s* attached to the experiment number shows the equilibrium was approached from the side of supersaturation, namely, by first shaking the amyl alcohol with a stronger sulphuric acid solution than that with which it was finally brought into equilibrium. All the experiments were made at 25°.

TABLE XI.—DATA RELATING TO THE DISTRIBUTION BETWEEN WATER AND AMYL ALCOHOL.

Expt. No.	C_W.	$10^3C_A/C_W$.
1	0.1752	8 996
2	0.1749	8.825
3*s*	0.1844	9.183
4*s*	0 1849	9.207
5	0.08340	7.142
6	0.08131	7.183
7*s*	0.09034	7.271
8*s*	0.09154	7.384
9	0.04484	6.093
10	0.04447	6.138
11*s*	0.04695	6.140
12*s*	0.04695	6.257
13	0.02216	5.347
14	0.02234	5.294
15*s*	0.02160	5.355
16*s*	0.02162	5.232

TABLE XII.—MEAN VALUES OF THE DISTRIBUTION RATIO.

C_W.	C_A/C_W.
0.0220	0.00531
0.0460	0.00617
0.0870	0.00725
0.1800	0.00906

It will be seen that the concentration (C_A) of the acid in the alcohol increases more rapidly than its concentration (C_W) in the water, corresponding to the increase in the proportion of un-ionized acid in the more concentrated aqueous solutions. The fact that the rate of that increase is so small—smaller even than in the case of hydrochloric acid at corresponding concentrations—is apparently significant, for it indicates that the un-ionized H_2SO_4 is formed out of two ions (H^+ and HSO_4^-) in analogy with diionic substances, instead of directly out of three ions (H^+, H^+, and $SO_4^{=}$), in analogy with triionic substances.[1]

PART II.—SOLUTIONS OF SODIUM HYDROGEN SULPHATE.

9. Transference Measurements.

By M. A. Stewart.

Transference experiments with sodium hydrogen sulphate should throw much light on the extent to which hydrosulphate ion ionizes into hydrogen ion and sulphate ion. Such experiments were therefore made with an approximately 0.1 formal solution of this salt at 25°.

a. Preparation and Analysis of the Solutions.—A solution of sulphuric acid approximately 1-formal was made up and titrated against ignited sodium carbonate. About 500 cc. of this acid solution were weighed out, and enough sodium carbonate was added to it to neutralize it to within 0.5 per cent. This solution was boiled to expel the carbon dioxide and the neutralization completed with sodium hydroxide, with methyl orange as indicator. (Sodium hydroxide was not used for the entire neutralization for the reason that it is not readily obtained so pure as the carbonate.) To this solution was then added a second portion of the original sulphuric acid solution, of the same weight as the first portion, and the mixture made up to ten liters. A second solution (No. 2) was afterwards prepared in the same way.

The solutions were analyzed: (1) by determining the sodium by evaporating, igniting, and weighing as Na_2SO_4; (2) by determining the sulphate as barium sulphate; and (3) by determining the hydrogen by titrating (by weight) with a standardized, approximately 0.2 formal, sodium hydroxide solution.

The mean results of the analyses of the sodium hydrogen sulphate solutions are as follows, the content being referred to 1000 grams of the solution:

	Mols. SO_4.	Mols. H.	Mols. Na.	Density at 25°/4°.
Solution No. 1..........	0.09889	0.09905	0.09886	1.0063
Solution No. 2..........	0.10090	0.10096	0.10083	1.0065

---

[1] The results of a distribution experiment made by shaking a 0.1015 formal solution of sodium hydrogen sulphate with amyl alcohol are also worth recording. It was found in this case that the value of C_A was 0.000299. Correcting the $NaHSO_4$ concentration to just 0.1000 formal, we get for C_A the value 0.000294; and interpolation of the data obtained for the acid itself shows that the sulphuric acid solution which would be in equilibrium with this same amyl-alcohol phase, and which would therefore contain un-ionized sulphuric acid at the same concentration as the 0.1000 formal sodium hydrosulphate is 0.0474 formal.

b. Description of the Apparatus and Method.—The apparatus used in these experiments was of the same form as that used earlier by Noyes.[1] It consisted of two glass U-tubes, each with one arm bent at right angles, joined together by a double band of rubber tubing. The inside diameter of the tubes used at first was about 3.5 cm. and the height about 37 cm. Smaller tubes, 2.5 cm. in diameter, with the other dimensions the same as before, were used later. The positive electrode was a polished platinum disk which would just fit loosely in the tube, and the negative electrode was a platinum spiral. A disk was used as anode, in order to give a large surface, so as to reduce the current density and prevent as far as possible the formation of decomposition products of sulphuric acid. The surface of the liquid at the cathode was kept at about two-thirds of the height of the tube, and the surface at the anode about 5 cm. above the top of the lower bend, with the anode about 1 cm. below the surface. The surface of the liquid in the anode limb was kept at this low position because the liquid around the anode tends to become heavier (due to the migration of sulphuric acid into it), so that to fill up that limb much above the bend would unnecessarily increase the quantity of solution. This position was maintained by connecting the anode arm with a small tube dipping beneath a column of water. All the openings were closed with rubber stoppers, but the liquid in the cathode arm was open to the outside air through a glass tube passing through the stopper. The middle portions of the solutions were removed through the small upright tubes on the middle arms. In order to make the joint between the U-tubes as tight as possible, a coating of vaseline was put over the rubber band and each side wound around with wire. The apparatus was immersed in a thermostat at 25° ± 0.02°, so that the horizontal middle part was covered by at least 3 cm. of water. Two silver coulometers were used, one on each side of the transference apparatus, in order to make sure that there was no leakage of the electric current.

After the electrolysis the solution was divided into an anode, a cathode, and a middle portion (represented by A, C, and M in the tables below), except that in the first experiment the middle portion was divided into three parts (M_A, M, and M_C).

The middle portion was titrated with a solution of sodium hydroxide containing 0.19816 equivalent NaOH per 1000 grams of solution, the content having been determined by titration against a standard sulphuric acid solution. The cathode and anode portions were also titrated with this sodium hydroxide solution; and, in addition, their contents in sulphate and in sodium were determined in the same way as was done with the original solution, the former by precipitating and weighing as barium sulphate and the latter by evaporating, igniting, and weighing as sodium sulphate. The determination of the sulphate was made in the portion of the solution that had already been titrated with sodium hydroxide.

---

[1] THIS JOURNAL, 23, 42 (1901).

c. Data of the Experiments.—Ten transference experiments were made, but in four of them the change in the middle portion was so large that the experiments were not completed. The results of the other six experiments are given in the following tables.

The headings of the columns are for the most part self-explanatory. The figures in columns II, IV, and V represent grams; those in VI, VII, VIII, and IX, milli-equivalents. In the case of Experiment No. 1, column VIII*a* contains the sum of the changes in the anode (A) and anode middle (M_A) portions or in the cathode (C) and cathode middle (M_C) portions.

TABLE XIII DATA OF THE TRANSFERENCE EXPERIMENTS

Experiment No. 1

Concentration of $NaHSO_4$: 0.00889 mol per 1000 grams. Time = 3.2 hours. Current = 0.060 ampere. Silver in coulometer: 758.5 mg.

I	II	III.	IV	V.	VI	VII	VIII.	VIIIa	IX
					Content of whole portion				
Portion	Weight of whole portion	Constituent determined	Weight of portion analyzed	Weight of NaOH solution, of $BaSO_4$, and of Na_2SO_4	Before electrolysis	After electrolysis	Change	Total change	Change per faraday
A	208.09	H	85.39	49.50	20.542	23.830	+3.288	+3.334	+474.4
		SO_4	85.39	2.0905	41.141	43.578	+2.437	+2.449	+348.4
		Na	117.99	0.7960	20.564	19.750	−0.814	−0.848	−120.7
		Na+H —SO_4	....	...	−0.035	+0.002			
M_A	161.15	H	161.15	80.79	15.914	15.960	+0.046		
		SO_4	161.15	3.7270	31.872	31.884	+0.012		
		Na	....	..	....	....	−0.034[1]		
M	165.89	H	165.89	82.93	16.382	16.383	+0.001		
M_C	181.74	H	181.74	90.76	17.947	17.930	−0.017		
		SO_4	181.74	4.2042	35.944	35.967	+0.023		
		Na	....	....	....	....	−0.040[1]		
C	334.78	H	122.82	55.07	33.066	29.654	−3.412	−3.429	−487.9
		SO_4	122.82	2.7337	66.226	63.753	−2.473	−2.450	−348.6
		Na	164.62	1.1925	33.103	34.117	+1.014	+1.054	+150.0
		Na+H —SO_4	....	....	−0.057	+0.018			

[1] Obtained by difference.

TABLE XIII—(*Continued*).

Experiment No. 2.

Concentration of $NaHSO_4$: 0.09889 mol per 1000 grams. Time = 3 hours. Current = 0.059 ampere. Silver in coulometer: 721.5 mg.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Portion.	Weight of whole portion.	Constituent determined.	Weight of portion analyzed	Weight of NaOH solution, of $BaSO_4$ and of Na_2SO_4.	Content of whole portion.			Change per faraday.
					Before electrolysis.	After electrolysis.	Change	
A	291.74	H	125 49	69.56	28.803	31.94	+3.14	+469.7
		SO_4	125 49	3.0164	57.688	59.99	+2.30	+344.1
		Na	154.54	1.0533	28.840	27.98	—0 86	—128.7
		Na+H—SO_4	....	....	—0.045	—0.07		
M	124.38	H	124.38	62 17	12.283	12.282	—0.001	
C	424.68	H	103.92	47.95	41.944	38.71	—3.23	—483.2
		SO_4	103.92	2.3334	84.070	81.58	—2.49	—372.5
		Na	157.85	1.1327	41.990	42.87	+0 88	+131 6
		Na+H—SO_4	....	....	0.136	0.00		

Experiment No. 3.

Concentration of $NaHSO_4$: 0.10090 mol per 1000 grams. Time = 4.5 hours. Current = 0.045 ampere. Silver in coulometer: 824.5 mg.

A	326.58	H	116.89	66.04	32.961	36.563	+3 602	471.5
		SO_4	116.89	2.8635	65.850	68.438	+2.588	338.8
		Na	174.82	1.2147	32.925	31.924	—1.001	131.0
		Na+H—SO_4	....	....	0.036	0.049		
M	123.57	H	123.57	62.99	12.474	12.482	+0 008	
C	388.33	H	131.93	60.86	39.209	35.499	—3.710	485.7
		SO_4	131.93	3.0040	78.333	75.652	—2.681	351.0
		Na	184.62	1.3583	39.166	40.195	+1.029	134.7
		Na+H—SO_4	....	....	0.042	0.042		

Experiment No. 4.

Concentration of $NaHSO_4$: 0.10090 mol per 1000 grams. Time = 4 hours. Current = 0.034 ampere. Silver in coulometer: 568.5 mg.

A	176.28	H	81.86	47.46	17.791	20.253	+2.462	+467.4
		SO_4	81.86	2.0236	35.543	37.276	+1.733	+329.0
		Na	86.49	0.5944	17.771	17.044	—0.727	—138.0
		Na+H—SO_4	....	....	0.019	0.021		
M	121.89	H	121.89	62.09	12.305	12.304	0.01	
C	215.12	H	94.46	42.38	21.722	19.125	—2.597	—493.0
		SO_4	94.46	2.1264	43.398	41.434	—1.964	—372.9
		Na	117.28	0.8684	21.699	22.409	+0.710	+134.8
		Na+H—SO_4	....	....	0.023	0.100		

TABLE XIII—(*Continued*).

Experiment No. 5.

Concentration of $NaHSO_4$: 0.10090 mol per 1000 grams. Time = 3 hours. Current = 0 050 ampere. Silver in coulometer: 607 4.

I	II.	III	IV.	V.	VI.	VII.	VIII.	IX
					Content of whole portion.			
Portion	Weight of whole portion	Constituent determined	Weight of portion analyzed	Weight of NaOH solution, of $BaSO_4$ and of Na_2SO_4.	Before electrolysis.	After electrolysis.	Change.	Change per faraday
A	182 45	H	75.31	43.84	18.413	21.047	+2.634	468.0
		SO_4	75.31	1.8680	36.785	38.712	+1 927	342.4
		Na	101 32	0 6962	18.393	17 638	-0.755	134 2
		Na+H - SO_4		..	0 021	0 027		
M	100 35	H	100 35	51 16	10 130	10 138	+0 008	
C	230.77	H	100 11	44 99	23.302	20.551	- 2 751	488.8
		SO_4	100.11	2 2580	46.553	44 534	—2 019	358.8
		Na	125 26	0 9269	23.276	24 024	+0 748	132 9
		Na+H SO_4	.	..	0.025	0 041		

Experiment No. 6.

Concentration of $NaHSO_4$: 0 10090 mol per 1000 grams Time = 2 hours. Current = 0 060 ampere. Silver in coulometer: 534.4 mg.

I	II.	III	IV.	V.	VI.	VII.	VIII.	IX
A	181.84	H	66.20	37 94	18.352	20.651	+2 299	464.3
		SO_4	66.20	1 6283	36.665	38.260	+1.595	322.1
		Na	110 30	0 7631	18.332	17 699	—0 633	127.8
		Na+H - SO_4	..	. .	+0.019	0.090		
M	118.14	H	118.14	60.15	11.926	11.920	—0.05	
C	215.80	H	89.38	40 40	21.790	19.329	—2.461	497.0
		SO_4	89 38	2.0208	43.532	41.745	—1.787	360.9
		Na	101.06	0.7473	21.766	22.450	+0.684	138.1
		Na+H - SO_4	...	....	+0.024	+0.034		

10. Summary of the Transference Results.

The results of the preceding experiments are summarized in the following table. The figures show the increase in the number of milliequivalents of the three constituents named in the heading in the anode and cathode portions when one faraday of electricity is passed at 25° through a solution containing approximately 0.1 formula weight of sodium hydrogen sulphate per liter. The "weighted mean" is derived from the means of the anode and cathode values by assigning to each a weight inversely proportional to the square of its average deviation ("A. D."). The "final values" are derived from the three weighted means upon the basis of the principle[1] that the increment of the equivalents of hydrogen must equal the difference of the increments of the equivalents of sulphate and of sodium ($\Delta H = \Delta(\frac{1}{2}SO_4) - \Delta Na$), by distributing the deviation from this principle upon the three separate values in inverse proportion to the square of their average deviations.

---

[1] This principle can be shown to be a consequence of the facts that one equivalent of hydrogen is produced at the anode by the electrolysis; that the only ions in

Table XIV.—Summary of the Transference Data.

Expt. No.	Hydrogen (ΔH). Anode.	Hydrogen (ΔH). Cathode.	Sulphate $\Delta(\frac{1}{2}SO_4)$. Anode.	Sulphate $\Delta(\frac{1}{2}SO_4)$. Cathode.	Sodium (ΔNa). Anode.	Sodium (ΔNa). Cathode
1	+474.4	−487.9	+348.4	−348.6	−120.7[1]	+150.0[1]
2	469.7	483.2	344.1	372.5	128.7	131.6
3	471.5	485.7	338.8	351.0	131.0	134.7
4	467.4	493.0	329.0	372.9	138.0	134.8
5	468.0	488.8	342.4	358.8	134.2	132.9
6	464.3	497.0	322.1[1]	360.9	127.8	138.1[1]
Mean	469.2	489.3	340.5	360.8	131.9	133.5
a. d.	2.6	2.9	5.3	8.0	3.3	1.3
A. D.	1.1	1.2	2.4	3.3	1.5	0.7
Weighted mean	478.4		347.5		133.2	
Final value	478.8		345.8		133.0	

11. Conductance Measurements.

Before discussing further the transference values, the results of some conductance measurements with sodium hydrogen sulphate will be presented. These measurements were made in a U-shaped conductance vessel with electrodes which were mechanically roughened, but not platinized.

The results are given in the following table, in which the "dilution" signifies the liters of solution in which one formula weight of $NaHSO_4$ was contained.

Table XV.—Formal Conductance of Sodium Hydrogen Sulphate at 25°.

Dilution.	Series 1.	Series 2.	Mean.	Barth.
10	261.60	261.73	261.67	...
20	297.00	....	297.00	...
40	337.78	337.68	337.73	336.8
80	381.42	....	381.42	380.7
160	424.94	424.58	424.76	423.0
320	463.48	463.10	463.30	463.0
640	494.40	494.60	494.50	497.0
1280	516.60	516.89	516.75	519.0
2560	530.74	531.20	530.97	...

the solution are H^+, Na^+, HSO_4^-, and $SO_4^{=}$; that the transference of each constituent is determined by that of these separate ions, as expressed by these equations:

$$\Delta H = 1 + HSO_4^- - H^+, \ \Delta Na = -Na^+, \text{ and } \Delta SO_4 = HSO_4^- + SO_4^{=};$$

and that the sum of all the equivalents of all the ions transferred must be unity:

$$H^+ + Na^+ + HSO_4^- + 2SO_4^{=} = 1.$$

From these equations there results by combination:

$$\Delta H = 2\,\Delta SO_4 - \Delta Na = \Delta(\tfrac{1}{2}SO_4) - \Delta Na.$$

[1] Omitted in the calculation, since their deviations are greater than 3 A. D.

Measurements of the conductance of this salt at 25° had previously been made by Barth.[1] His values, reduced from Siemens' units to reciprocal ohms and interpolated graphically (from a plot of Λ against log v) for the dilutions at which our measurements were made, are given in the last column of the table.

12. Concentrations of the Sodium Ion and Hydrogen Ion Derived from the Transference and Conductance Data.

A simple interpretation of the transference results is obtained through the following considerations. Let C_H, C_{Na}, C_{SO_4}, and C_{HSO_4} represent the formal concentrations in the sodium hydrogen sulphate solution of the ions denoted by the subscripts; let Λ_H, Λ_{Na}, Λ_{SO_4}, and Λ_{HSO_4} represent the equivalent conductances of those ions, and N_H, N_{Na}, and N_{SO_4} the equivalents of hydrogen, sodium, and sulphate transferred for each faraday of electricity passed; and let L represent the specific conductance of the solution. Then, since the number of equivalents of any ion transferred is equal to the ratio of the actual conductance of that ion to that of the solution, and since hydrogen is transferred in the two forms, H^+ and HSO_4^-, and sulphate in the two forms HSO_4 and SO_4 , we have the relations

$$N_{Na} = \frac{C_{Na}\Lambda_{Na}}{10^3\,L} \quad (9); \quad N_H = \frac{C_H\Lambda_H - C_{HSO_4}\Lambda_{HSO_4}}{10^3\,L} \qquad (10);$$

and

$$N_{SO_4} = \frac{2C_{SO_4}\Lambda_{SO_4} + 2C_{HSO_4}\Lambda_{HSO_4}}{10^3\,L}. \qquad (11)$$

In these equations we may substitute $C\Lambda$ for 10^3L, introduce the values $N_{Na} = 0.133$, $N_H = 0.521$, $N_{SO_4} = 0.346$, $\Lambda = 261.7$, $\Lambda_{Na} = 51$, $\Lambda_{SO_4} = 79$, $\Lambda_H = 365$ or 348 (see Section 2), and $\Lambda_{HSO_4} = 39.5$,[2] and solve for the ratios C_{Na}/C, C_H/C, etc. We thus obtain from equations (9) and (11),

$$\frac{C_{Na}}{C} = 0.68, \text{ and } \frac{2C_{SO_4}}{C} + \frac{C_{HSO_4}}{C} = 1.15.$$

Since the sums of the equivalent concentrations of all the positive and negative ions must be equal, we have $C_{Na} + C_H = 2C_{SO_4} + C_{HSO_4}$, and therefore also

$$\frac{C_{Na}}{C} + \frac{C_H}{C} = 1.15, \text{ and } \frac{C_H}{C} = 0.47.$$

A value of C_H/C lying between certain not very wide limits can be obtained from equation (10) also, since the second term in its last member is a much smaller quantity than the first term which contains C_H/C. Placing C_{HSO_4}/C equal to zero as one limit and equal to 0.5 as the other (which last is the largest value, consistent with that of C_H/C, which it can have), one obtains

---

[1] *Z. physik. Chem.*, 9, 182 (1892).

[2] In Section 3 Λ_{HSO_4} was found to be about 40 when Λ_H was taken as 365, and about 35 when Λ_H was taken as 348. We have assumed in these calculations $\Lambda_{HSO_4} = \frac{1}{2}\Lambda_{SO_4} = 39.5$, since equation (11) can then be solved directly for $2C_{SO_4} + C_{HSO_4}$. The error arising from this uncertainty is almost surely less than that arising from the errors in the transference data.

$$\frac{C_H}{C} = \begin{cases} 0.37 \text{ for } \Lambda_H = 365 \text{ and } C_{HSO_4}/C = 0.0 \\ 0.43 \text{ for } \Lambda_H = 365 \text{ and } C_{HSO_4}/C = 0.5 \end{cases}$$

$$\text{or} \quad \frac{C_H}{C} = \begin{cases} 0.39 \text{ for } \Lambda_H = 348 \text{ and } C_{HSO_4}/C = 0.0 \\ 0.45 \text{ for } \Lambda_H = 348 \text{ and } C_{HSO_4}/C = 0.5 \end{cases}.$$

Taking the mean (0.41) of these four values and combining it with the value (0.47) obtained from equation (11), we get as the final value

$$C_H/C = 0.44.$$

Although C_{HSO_4}/C can be definitely calculated by equation (10), by substituting in it the value of C_H/C derived from equation (11), yet the result (0.85 for $\Lambda_H = 365$ or 0.65 for $\Lambda_H = 348$) has no significance, since it is seriously affected by the accumulated error resulting from the two successive subtractions of terms much larger than that containing C_{HSO_4}/C.

It is therefore only the values of C_H/C and C_{Na}/C that can be derived with a fair degree of accuracy from the transference and conductance data, unless some additional assumption be made. It is of some interest to compare the values of these quantities obtained above with the results of Noyes and Eastman[1] for 0.1 formal potassium hydrogen sulphate at 18°, which were derived from conductance data alone with the help of estimates as to the concentrations of the un-ionized substances (K_2SO_4, H_2SO_4, and $KHSO_4$) in the solution, based upon analogies with other substances of these same types. Their values are $C_H/C = 0.51$ and $C_{Na}/C = 0.63$, while ours are $C_H/C = 0.44$ and $C_{Na}/C = 0.68$.

13. The Hydrogen-Ion Concentration Derived from Catalysis Experiments.

A value of the hydrogen-ion concentration may also be derived from the catalysis experiments made at 35° by Kay.[2] He found that the specific reaction rate of the hydrolysis of ethyl acetate under the influence of 0.1 formal sodium hydrogen sulphate is 32.4. This becomes 31.0 when corrected in accordance with his experiments for the influence of the neutral-salt ions (the Na^+ and $SO_4^=$) upon the rate. Dividing this value by the specific reaction rate per equivalent of hydrochloric acid (708) at the corresponding concentration, as determined by him, we get 0.0448 as the concentration of the hydrochloric acid solution which has the same catalytic effect as the 0.1 formal sodium hydrogen sulphate.[3]

---

[1] *Carnegie Institution Publications*, 63, 276 (1907).

[2] *Proc. Royal Soc. Edinburgh*, 22, 491 (1898).

[3] Kay found the effect of $LiHSO_4$ to be nearly identical with that of $NaHSO_4$, and that of $KHSO_4$ to be about 2 per cent. smaller.

Taking the ionization of the acid as 95 per cent., we find *0.416* to be the value of C_H/C in the sulphate solution at 35°. The value derived from the transference and conductance measurements was 0.44 at 25°. The agreement is seen to be fairly close, especially in view of the fact that C_H/C decreases rapidly with rising temperature.

Noyes and Eastman have already pointed out that their value of C_H/C at 100° (0.31 at 0 01 formal) agrees well with that (0.315) derived by Trevor[1] from sugar inversion experiments at 100°.

14. Concentrations of the Other Constituents.

Although unfortunately, on account of lack of accuracy, it was not possible to calculate the relative concentrations of sulphate ion and hydrosulphate ion from the transference and conductance data alone, yet we are in a better position to estimate these concentrations than were Noyes and Eastman, for there is now available not only a more directly determined value of C_H/C, but also, in addition, a fairly reliable value of C_{Na}/C. From the latter (0 68) one can at once conclude that the sum of the concentrations of the un-ionized salts ($2C_{Na_2SO_4} + C_{NaHSO_4}$) is 0.32, and no considerable error can result if we distribute this value between the two salts in the proportion $C_{Na_2SO_4} : 2C_{SO_4} = C_{NaHSO_4} : C_{HSO_4}$, in accordance with the principle that in a mixture with a common ion the un-ionized fraction of a unibivalent salt is approximately twice as large as that of a uni-univalent salt. (In making this distribution any probable value may be assigned provisionally to C_{SO_4}/C and C_{HSO_4}/C, such as 0.44 and 0.22, and the operation can then be repeated with the more accurate values of the latter quantities subsequently obtained.) If further we make the assumption, substantiated by Noyes and Eastman (see Section 7), that sulphuric acid with respect to its first hydrogen and hydrochloric acid are equally ionized under corresponding conditions, we can estimate the un-ionized H_2SO_4 present in the solution and finally obtain by subtraction the concentrations of the HSO_4^- and SO_4^{--} ions. The results of such a calculation are given in the following table:

TABLE XVI.—CONCENTRATIONS OF THE CONSTITUENTS IN 0.1 FORMAL SODIUM HYDROGEN SULPHATE SOLUTION AT 25°.

C_{Na}/C	0.68	C_{NaHSO_4}/C	0.08
C_H/C	0.44	$C_{Na_2SO_4}/C$	0.12
C_{HSO_4}/C	0.44	$C_{H_2SO_4}/C$	0.02
C_{SO_4}/C	0.34		

It is of interest to calculate from these data and also from the corresponding data given in Table X for sulphuric acid the values of the product $C_H C_{SO_4}/C_{HSO_4}$, which, if the mass-action law held, would be the ionization constant for the second hydrogen of sulphuric acid. The values of this product at 25° are found to be 0.034, 0.031, and 0.022, using the data for 0.1 formal $NaHSO_4$, 0.05 formal H_2SO_4, and 0.025 formal H_2SO_4, respectively.[1] The "ionization constant" at these concentrations (0.025 — 0.1 formal) may therefore be taken in round numbers at 3×10^{-2}. The rough agreement of the values derived from the independent and widely different data for sulphuric acid and its acid salt is welcome evidence of the approximate correctness of the computed concentrations of the sulphate ion and hydrosulphate ion in the solutions, the computation of which was based in both cases, it must be remembered, upon the only indirectly substantiated principle that the hydrogen of hydrochloric acid and the first hydrogen of sulphuric acid are equally ionized under corresponding conditions.

---

[1] *Z. physik. Chem.*, 10, 342 (1892).

SUMMARY.

It has been shown in Section 1 of this article that in the case of a dibasic acid like sulphuric acid the hydrogen-ion concentration (C_H) can be derived from the freezing-point lowering, or from any other property which gives the value of the mol number i, by the relation $C_H/C = i - 1$, where C represents the formal concentration of the acid (that is, the number of formula weights of H_2SO_4 per liter of solution). The values of C_H/C at 0° so derived from the existing freezing-point data have been presented.

Noyes and Eastman have previously shown that there can be derived from conductance data alone not very widely divergent maximum and minimum values of the hydrogen-ion concentration in sulphuric acid, corresponding to the two limiting cases where the only negative ion present is $SO_4^{=}$ and where it is HSO_4^-. In their calculations it was, however, necessary to assume a value for Λ_{HSO_4}, the equivalent conductance of hydrosulphate ion, the assumption made being that its conductance is equal to that of acetate ion, which has a similar molecular complexity. It has been shown that any such assumption can be dispensed with, if with the conductance data there be combined the transference data for the acid. In this way, using the existing transference data and the conductance data at 25° and 0° determined in this laboratory and presented in Section 2, limiting values of C_H/C at these temperatures have been calculated.

Incidentally, there have been derived through a consideration of the existing conductance data at 0° the best values to adopt for the equivalent conductance at 0° of certain ions. These values are $\Lambda_K = 40.3$, $\Lambda_{Cl} = 41.1$, $\Lambda_{SO_4} = 42.8$, and $\Lambda_H = 224$. The last value is much lower than that (240) estimated by Johnston.[2]

It has been shown in Section 3 that the transference and conductance data enable the value of Λ_{HSO_4} at 25° and 0° to be approximately calculated, provided it be true that the hydrosulphate-ion is present in the sulphuric acid solution in considerable quantity, so that its conductance may enter as a factor. The values obtained (35 to 40 at 25°) are not far from one-half of that of Λ_{SO_4} (79 at 25°).

---

[1] The values at 0° are 0.061 for 0.05 formal H_2SO_4 and 0.042 for 0.025 formal H_2SO_4.

[2] This Journal, 31, 1015 (1909).

From a consideration of the relative catalytic effects of sulphuric and hydrochloric acids on the hydrolysis of cane sugar at 25°, as determined by Ostwald, and on that of ethyl acetate at 35° as determined by Kay, values of the hydrogen-ion concentration (C_H/C) have also been calculated (see Section 4).

A new isohydric method of determining the hydrogen-ion concentration has been described in Section 5. It consists in determining by experiment the relative concentrations of hydrochloric acid and of sulphuric acid which drive back the ionization of picric acid to the same extent, the condition of equal ionization of the picric acid being ascertained by shaking the aqueous solution with benzene, into which the un-ionized picric acid distributes itself.

The values of C_H/C at various concentrations at 0° and 25°, obtained by these various methods, will be found in Table IX on page 1146.

To derive the concentrations of the other constituents from these values of the hydrogen-ion concentration, the latter must be combined with some further knowledge or data relating to those constituents. Noyes and Eastman, through a study of the conductance of sulphuric acid and potassium hydrogen sulphate through a wide range of temperature, have made it highly probable that under corresponding conditions the first hydrogen of sulphuric acid is equally dissociated with that of hydrochloric acid. Upon the basis of this principle the concentration of the un-ionized H_2SO_4 was estimated by Noyes and Eastman, and, from this concentration and that of the hydrogen ion the concentrations of the other two constituents, the sulphate ion and hydrosulphate ion, were obtained by them by subtraction. We have made similar calculations, using the values of the hydrogen-ion concentration derived in this paper. The results, which will be found in Table X on page 1148, show that sulphate ion and hydrosulphate ion are both present in large proportions at medium concentrations, that the latter is present in much larger quantity at 0.05 formal and the former at 0.005 formal, and that at 0.05 formal the ratio C_{HSO_4}/C_{SO_4} increases greatly between 0° and 25°. It will also be seen that the hydrogen-ion concentration decreases markedly within the same temperature interval.

Experiments have been described in Section 8 upon the distribution of sulphuric acid between water and amyl alcohol. The ratio C_A/C_W of the concentration of the acid in the alcohol to that in the water was found to increase from 0.0053 for $C_W = 0.022$ to 0.0091 for $C_W = 0.180$, corresponding to an increase in the proportion of un-ionized sulphuric acid in the aqueous solution. The rate of this increase is somewhat smaller even than in the case of hydrochloric acid, indicating that the un-ionized H_2SO_4 is formed out of two ions (H^+ and HSO_4^-), in analogy with di-ionic substances, instead of directly out of three ions (H^+, H^+, and $SO_4^{=}$) in analogy with tri-ionic salts.

Determinations were also made of the transference of sodium, of hydrogen, and of sulphate occurring during the electrolysis of a 0.1 formal solution of sodium hydrogen sulphate at 25°. The results are summarized in Table XIV, on page 1156. Measurements were also made upon the conductance of this salt at various concentrations at 25°. By combining the transference and conductance data the concentrations of the sodium ion and hydrogen ion in the 0.1 formal solution were calculated (in Section 12). The values so obtained are $C_{Na}/C = 0\ 68$, and $C_H/C = 0.44$.

It has also been shown (in Section 13) that the experiments of Kay on the catalysis of ethyl acetate by 0.1 formal sodium hydrogen sulphate at 35° furnish an independent means of determining the hydrogen-ion concentration, and that the value of C_H/C derived therefrom is 0 416, which agrees well with that (0.44) derived from the transference experiments.

From the values of C_H/C and C_H/C_{Na} derived from the transference and conductance data the concentrations of the other constituents in the 0.1 formal $NaHSO_4$ were computed (in Section 14) with the help of the principle above referred to in regard to the ionization of the first hydrogen of sulphuric acid. In this way C_{HSO_4}/C was found to be 0.44 and C_{SO_4}/C to be 0.34 (see Table XVI).

From these data and also from the corresponding ones for 0.05 formal H_2SO_4 the values of the product $C_HC_{SO_4}/C_{HSO_4}$, the ionization constant of the second hydrogen of sulphuric acid, were calculated to be 0.034 and 0.031, respectively, or in round numbers 3×10^{-2} at concentrations 0.025 to 0.1 formal.

BOSTON, July, 1910.

ON SURFACE ENERGY AND SURFACE TENSION.

BY J. E. MILLS AND DUNCAN MACRAE.

Received July 25, 1910.

In an article by Whittaker[1] "On the Theory of Capillarity," it was shown that the following empirical relation was apparently true: "*The surface energy of a liquid in contact with its own vapor at any temperature is proportional to the product of the internal latent heat and the* (*absolute*) *temperature.*"

The proposed relation and further related applications and inferences have since been discussed by Kleeman in a number of papers.[2]

---

[1] *Proc. Roy. Soc.*, **81**, 21 (1908).

[2] *Phil. Mag.*, **18**, 39, 491, 901 (1909); **19**, 783 (1910)

Some explanation of the relation proposed is perhaps necessary. Particles in the interior of a liquid are attracted by the surrounding molecules equally in every direction; but particles on, or near, the surface are attracted only, or as a resultant, inward, in a direction perpendicular to the surface. When the area of the surface of a liquid is increased, work is therefore done against the molecular forces in bringing additional molecules within the surface layer. If the surface of a liquid is actually increased—as in blowing a soap bubble—it will be found that as the surface increases in size under the action of the externally supplied force (the pressure of the air blown within the bubble), the surface layer of the liquid becomes at the same time colder. Heat is absorbed from the surrounding bodies in order to raise the temperature of the surface film to the initial temperature. Therefore the total energy necessary to increase the surface area is supplied partly as mechanical (external) work and partly as heat energy. If E represents the total energy per square centimeter of surface layer, γ, the necessary mechanical work performed in making this surface, and T the absolute temperature, we have from Helmholtz's free energy equation the relation first stated by Lord Kelvin,

$$1. \qquad E = \gamma - T\frac{d\gamma}{dT},$$

where $-T\,d\gamma/dT$ represents the amount of heat energy absorbed from the surrounding bodies. The mechanically supplied surface energy, γ, in ergs per square centimeter, is numerically equal to the surface tension per linear centimeter in dynes.

The heat of vaporization necessary to change a liquid into a vapor is expended in two ways: *first*, in pushing back the external pressure as the liquid expands, and *second*, in doing certain internal work within the liquid. The first amount of energy is easily calculated and when subtracted from the total leaves the so-called "internal heat of vaporization." This internal heat of vaporization, λ, can be calculated from the thermodynamical relation discovered by Clausius and Clapeyron,

$$2. \qquad \lambda = \left(T\frac{dP}{dT} - P\right)(V - v);$$

here P denotes the vapor pressure, and v and V denote the volume of liquid and its saturated vapor, respectively.

The proposed relation of Whittaker states that

$$3. \qquad \frac{E}{T\lambda} = \text{constant},$$

where E is obtained from equation 1 and λ from equation 2.

Whittaker himself stated that the above empirical relation, being yet without theoretical basis, and being based only on the behavior of five substances over a limited range of temperature, must be received with caution until further comparison with experimental results was possible.

It seemed to the authors desirable, for the reasons mentioned below, to re-examine the experimental basis for the proposed relation.

First.—The values of the internal heat of vaporization used by Whittaker were taken from a paper by one of us[1] and these values have been lately revised. The revision was made necessary by the changes made by Dr. Sydney Young in the original data used for the calculation of these values. These changes were usually small, but extensive, and affected principally the volumes of the saturated vapor at the lower temperatures and the vapor pressure.[2]

Second.—Whittaker, due to the increasing uncertainty in the values for the internal heat of vaporization, and in $d\gamma/dT$ as the critical temperature was approached, did not extend his study of the relation given in equation 3 nearer the critical temperature than 40 or 50°. While it is true that the data become increasingly uncertain, it is also true that λ, E, γ, and $d\gamma/dT$, when plotted against the temperature, give early straight lines over the range of temperature investigated by Whittaker. It becomes of very greatly increased importance therefore to carry the study of equation 3 nearer the critical temperature.

Third.—Whittaker obtained his values of $d\gamma/dT$ from the values for γ as given by Ramsay and Shields.[3] Now they concluded from an apparently sufficient experimental basis that the surface tension, γ, could be expressed for non-associated liquids, as were those investigated by Whittaker, by the equation

$$4. \qquad \gamma(Mv)^{2/3} = k(\tau - d),$$

where τ represents degrees counted from the critical temperature, and k and d are constants, k being approximately 2.12, and d varying with the different substances investigated from 5.9 to 8.5. Mv is the molecular volume of the liquid. Equation 4 is true nearly to the critical temperature, and it is clear that the function $-d\gamma/dT$ must therefore decrease continuously and consistently with increase of temperature; that is, for non-associated liquids $-d\gamma/dT$, when plotted against the temperature, must neither increase nor give a line of double curvature. An examination of the values of $d\gamma/dT$ given by Whittaker for carbon tetrachloride, benzene, and chlorobenzene show that his values do not strictly obey the above statement and seem too greatly influenced by the individual errors of observation. We have changed, therefore, in the tables below, usually only very slightly, some of the values of $d\gamma/dT$ as given by Whittaker for the above-mentioned substances.

Whittaker states on page 23 of the article cited that "A point is at length reached, about 180° below the critical point, at which E is stationary, and thenceforward E diminishes as the temperature decreases—a somewhat surprising result. These changes in E are identical with the changes of the function $T\lambda$, which has its stationary point at the same temperature as E." We consider this statement to be in error as regards the behavior of the surface energy so far as non-associated liquids are concerned. The remark seems true for associated liquids. For confirmation of our point of view it is sufficient to cite the form of the surface tension curves as shown in the paper by Ramsay and Shields, and the values of the internal heat of vaporization as given in the papers by Mills already cited.

---

[1] Mills, *J. Phys. Chem.*, **8**, 383 (1904); **10**, 1 (1906).

[2] Arrhenius number of *Z. physik. Chem.*, **70**, 620 (1910). *Scientific Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

[3] *Phil. Trans. Roy. Soc.*, **184A**, 647 (1893).

Fifth.—We found data available for a study also of ethyl acetate, and for the supposedly associated liquids, water, acetic acid, and methyl and ethyl alcohols.

The data and the results obtained are given in the tables below. The surface tension, γ, was obtained from the measurements of Ramsay and Shields.[1] The values of $d\gamma/dT$ were derived from the measurements of γ given, and were smoothed in accordance with the observations above made. The values of $d\gamma/dT$ given by Whittaker were used for ethyl ether and methyl formate at the lower temperatures, and his values were not greatly changed for carbon tetrachloride and benzene. The values for E were obtained from the data given by the use of equation 1. The

TABLE I.—ETHYL OXIDE.

t° C.	γ.	$-d\gamma/dT$.	E.	λ	$10^4E/T\lambda$.
20	16.49	..	....	80.04	....
40	14.05	0.112	49.1	75.02	20.9
50	12.94	0.1115	48.9	72.66	20.8
60	11.80	0.110	48.4	70.40	20.6
70	10.72	0.108	47.8	67.81	20.6
80	9.67	0.106	47.1	65.40	20.4
00	8.63	0.1035	46.1	62.89	20.2
100	7.63	0.1015	45.5	60.40	20.2
110	6.63	0.0995	44.7	57.53	20.3
120	5.65	0.097	43.8	54.53	20.4
130	4.69	0.094	42.6	51.43	20.6
140	3.77	0.0905	41.1	48.13	20.7
150	2.88	0.086	30.3	44.30	21.0
160	2.08	0.080	36.7	39.81	21.3*
170	1.33	0.071	32.8	34.31	21.6*
180	0.64	0.058	26.9	27.36	21.7*
185	0.38	0.0495	23.0	22.99	21.8*
190	0.16	0.040	18.7	16.59	24.3*
193	0.04	...	....	9.71	....
193.8	0	....	....	0	....
190	Mills	....	...	17.68	22.8*
190	Dieterici	...		17.44	23.2*

---

[1] *Phil. Trans.*, 184A, 647 (1893); *Z. physik. Chem.*, 12, 433 (1893).

values given for λ were calculated by Mills and have been partially published.[1] Details and references will be found in that paper. The complete data will be published later.

We have, except for the alcohols, averaged the values of the constant $10^4E/T\lambda$ for each substance down to the values marked with an asterisk, and have marked with an asterisk all values differing from the mean values so obtained by more than 3 per cent. The mean values are given in Table XI.

Considering first the non-associated substances, it will be seen that the "constant" decreases to the extent of 3 per cent. or more from its value at the lowest temperature to a minimum value, and then rises in value until the critical temperature is reached. This consistent behavior of the constant tends strongly to show that it is not a true constant. A closer examination of the data tends to confirm this belief.

For the divergence of the "constant" from constancy cannot be due to the values used for the internal heats of vaporization. One of us has made an extended and close study[2] of the internal heat of vaporization both of the substances at present under investigation and of other substances. From the discussion and data given in the papers cited we feel certain

TABLE II.—CARBON TETRACHLORIDE.

t° C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	25.68	....	....	....	....
80	18.71	. ..	..	41.64	. .
90	17.60	0.1115	58.1	40.72	39.3*
100	16.48	0.110	57.5	39.64	38.9
110	15.41	0.1085	57.0	38.53	38.6
120	14.32	0.107	56.4	37.48	38.3
130	13.27	0.105	55.6	36.35	38.0
140	12.22	0.103	54.8	35.27	37.6
150	11.21	0.1015	54.1	34.19	37.4
160	10.22	0.100	53.5	33.28	37.2
170	9.24	0.098	52.6	32.21	36.9
180	8.26	0.0965	52.0	30.83	37.2
190	7.28	0.095	51.3	29.52	37.5
200	6.34	0.093	50.3	28.22	37.7
210	5.40	0.0915	49.6	26.83	38.3
220	4.47	0.090	48.8	25.35	39.0
230	3.56	0.0870	47.3	23.73	39.6*
240	2.74	0.0825	45.1	21.91	40.1*
250	1.93	0.076	41.7	19.85	40.2*
260	1.20	0 067	36.9	17.15	40.4*
270	0.59	...	. ..	13.62	..
283 15	0	.	....	0	....
260	Mills		....	16.78	41.2*
260	Dieterici		. ..	16.97	40.8*

---

[1] THIS JOURNAL, 31, 1099 (1909).

[2] Mills, *Ibid.*, 31, 1099 (1909). *J. Phys. Chem.*, 13, 512 (1909).

TABLE III.—BENZENE.

$t°$ C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$
80	20.28	0.116	61.2	86.70	20.0
90	19.16	0.116	61.3	84.69	19.9
100	18.02	0.116	61.3	82.37	20.0
110	16.86	0.115	60.9	79.98	19.9
120	15.71	0.1145	60.7	77.39	20.0
130	14.57	0.1125	59.9	75.45	19.7
140	13.45	0.1105	59.1	73.45	19.5
150	12.36	0.108	58.0	71.34	19.2
160	11.29	0.106	57.2	69.48	19.0
170	10.20	0.104	56.3	67.25	18.9
180	9.15	0.102	55.4	65.21	18.8
190	8.16	0.100	54.5	62.51	18.8
200	7.17	0.098	53.5	59.75	18.9
210	6.20	0.096	52.6	57.04	19.1
220	5.25	0.094	51.5	53.76	19.4
230	4.32	0.091	49.9	50.30	19.7
240	3.41	0.087	48.1	46.53	20.1*
250	2.56	0.083	46.0	42.46	20.7*
260	1.75	0.0785	43.6	37.55	21.8*
270	0.99	0.073	40.6	31.49	23.7*
275	0.66			.	. .
280	0.29			23.45	. .
288.5	0			0	. .
270	Mills			31.47	23.7*

Dieterici not calculated at 270°, but at 260° = 37.52 and at 280° = 23.70

TABLE IV.—CHLOROBENZENE.

$t°$ C.	γ.	$-d\gamma/dT$	E.	λ	$10^4E/T\lambda$.
150	17.67	0.100	60.0	65.45	21.7
160	16.62	0.0995	59.7	64.14	21.5
170	15.67	0.0995	59.8	62.87	21.5
180	14.66	0.099	59.5	61.67	21.3
190	13.69	0.0985	59.3	60.06	21.3
200	12.72	0.0970	58.6	58.50	21.2
210	11.75	0.0960	58.1	56.87	21.1
220	10.81	0.0945	57.4	55.55	21.0
230	9.88	0.093	56.7	53.90	20.9
240	8.94	0.0915	55.9	52.25	20.9
250	8.04	0.090	55.1	50.37	20.9
260	7.14	0.0875	53.8	48.17	21.0
270	6.27	0.0855	52.7	45.80	21.2
280	5.40	0.0825	. .	. .	. .
290	4.54	0.080		.	.
300	3.79	0.0765	. .	. .	. .
310	3.05	0.073	. . . .	.	
320	2.35	0.069	. . .	.	
333	1.47	. . .		.	.
359.1	0	. . . .	. . .	. . .	. . .

TABLE V.—METHYL FORMATE.

$t°$ C.	γ.	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	24.62	. ..	....	....	...
30	23.09	0.153	69.4	104.38	21.9
40	21.56	0.151	68.8	101.16	21.7
50	20.05	0.149	68.2	98.18	21.5
60	18.58	0.147	67.5	94.74	21.4
70	17.15[1]	0.145	66.9	91.43	21.3
80	15.70	0.143	66.2	88.31	21.2
90	14.29	0.141	65.5	85.25	21.2
100	12.90	0.139	64.6	81.83	21.2
110	11.52	0.1365	63.8	78.96	21.1
120	10.18	0.134	62.9	75.87	21.1
130	8.86	0.1315	61.8	71.95	21.3
140	7.54	0.128	60.4	68.10	21.5
150	6.30	0.124	58.8	64.03	21.7
160	5.06	0.119	56.6	59.28	22.0
170	3.90	0.1125	53.7	54.41	22.3*
180	2.81	0.105	50.4	48.64	22.9*
190	1.78	0.096	46.2	41.93	23.8*
200	0.87	0.086	41.5	33.18	26.5*
210	0.06	. .		19.58	
214.0	0			0	
200	Mills			35.10	25.0*
200	Dieterici	.		35.04	25.0*

TABLE VI.—ETHYL ACETATE.

$t°$ C.	γ	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$
20	23.60	. .	....	.	
80	16.32	0.1185	58.1	78.25	21.1
90	15.14	0.117	57.6	76.40	20.8
100	13.98	0.115	56.9	74.36	20.5
110	12.84	0.113	56.1	72.13	20.3
120	11.75	0.111	55.4	69.64	20.2
130	10.66	0.109	54.6	66.84	20.3
140	9.57	0.107	53.8	64.42	20.2
150	8.52	0.1045	52.7	61.38	20.3
160	7.48	0.1025	51.9	58.36	20.5
170	6.47	0.100	50.8	55.71	20.6
180	5.51	0.097	49.4	52.68	20.7
190	4.54	0.093	47.6	49.48	20.8
200	3.64	0.089	45.7	46.11	21.0
210	2.80	0.0835	43.1	42.08	21.2
220	1.96	0.077	39.9	37.11	21.8*
230	1.18	0.069	35.9	31.32	22.8*
240	0.49	0.060	31.3	23.55	25.9*
245	0.21	....	....	18.00	. . .
250.1	0	.	....	0	....
240	Mills	. . .	....	24.78	24.6*
240	Dieterici	. . .	....	24.32	25.1*

[1] Misprinted in the original paper by Ramsay and Shields.

that the heats of vaporization given are correct to within 2 per cent. except as the critical temperature is approached. Nearly always they are correct to within 1 per cent. Now as the critical temperature is approached, it is true, as shown in the papers cited, that the internal heat of vaporization as usually calculated by the use of equation 2, and as given in this paper, is too small. But the error thus caused is not nearly great enough to account for the great increase in the value of the constant.

TABLE VII. WATER

$t°$ C	γ	$d\gamma/dT$	E.	λ	$10^4E/T\lambda$.
0	73.21	0.122	106.5	565.0	6.90
10	71.94	0.131	109.0	559.3	6.89
20	70.60	0.1385	111.2	552.5	6.87
30	69.10	0.1475	113.8	545.8	6.88
40	67.50	0.155	116.0	539.2	6.88
50	65.98	0.162	118.3	532.4	6.88
60	64.27	0.168	120.2	525.4	6.87
70	62.55	0.174	122.2	518.4	6.87
80	60.84	0.179	124.0	511.4	6.87
90	58.92	0.1835	125.5	504.5	6.85
100	57.15	0.188	127.3	497.1	6.87
110	55.25	0.192	128.8	489.2	6.87
120	53.30	0.196	130.3	481.0	6.89
130	51.44	0.200	132.0	472.9	6.92
140	49.42	0.204	133.7	465.0	6.96

TABLE VIII. ACETIC ACID.

$t°$ C	γ	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	23.46	. .	. .	79.17	....
130	16.18	0.083	49.6	85.09	14.5
140	15.32	0.085	50.4	83.62	14.6
150	14.46	0.0865	51.0	82.37	14.6
160	13.58	0.088	51.7	81.14	14.7
170	12.71	0.089	52.1	81.85	14.4
180	11.77	0.090	52.5	79.01	14.7
190	10.93	0.091	53.1	77.97	14.7
200	10.05	0.092	53.6	76.72	14.8
210	9.11	0.0923	53.7	75.32	14.8
220	8.22	0.0927	53.9	73.25	14.9
230	7.28	0.0930	54.1	71.44	15.0
240	6.36	0.0930	54.1	69.54	15.1
250	5.40	0.0930	54.0	67.05	15.4*
260	4.48	0.0915	53.2	64.00	15.6*
270	3.59	0.0885	51.6	60.37	15.8*
280	2.71	0.084	49.2	55.97	15.9*
290	1.92	0.0785	46.1	50.32	16.3*
300	1.16	0.0710	41.8	42.97	17.0*
310	0.49	....	....	33.06	....
320	0.32	....	....	18.27	....
321.65	0	....	....	0	....

TABLE IX.—METHYL ALCOHOL.

$t°$ C	γ	$-d\gamma/dT$.	E.	λ.	$10^4E/T\lambda$.
20	23.02	. . .	. . . .	266.5	. . . .
70	17.64	.	. . . .	244.4	. . . .
80	16.70	0.0905	48.6	238.5	5.77
90	15.72	0.093	49.5	232.1	5.87
100	14.80	0.0955	50.4	225.2	6.00
110	13.85	0.098	51.4	218.3	6.14
120	12.88	0.1005	52.4	211.0	6.32
130	11.84	0.103	53.3	203.2	6.51
140	10.79	0.1055	54.4	195.4	6.74
150	9.77	0.108	55.4	185.6	7.06
160	8.65	0.1105	56.5	178.2	7.32
170	7.53	0.113	57.6	168.5	7.71
180	6.41	0.1155	58.7	158.1	8.19
190	5.23	0.117	59.4	147.5	8.70
200	4.05	0.117	59.4	134.9	9.31
210	2.93	0.114	58.0	119.5	10.05
220	1.80	0.108	55.0	99.6	11.21
230	0.77	0.093	47.5	74.6	12.67
234	0.42	. .	. . . .	61.9	. . .
236	0.27	.	. . . .	54.4	. . .
240.0	0	. . .	. . . .	0	. . .

TABLE X.—ETHYL ALCOHOL.

$t°$ C	γ	$-d\gamma/dT$.	E.	λ	$10^4E/T\lambda$.
20	22.03	. . . .	. . . .	208.0	. . . .
40	20.20	0.0873	47.5	205.3	7.39
60	18.43	0.091	48.7	199.2	7.35
80	16.61	0.0943	49.9	191.6	7.38
90	15.63	0.096	50.5	186.6	7.45
100	14.67	0.098	51.2	181.8	7.55
110	13.69	0.0995	51.8	174.9	7.73
120	12.68	0.1015	52.6	168.8	7.92
130	11.63	0.103	53.1	162.1	8.14
140	10.59	0.105	53.9	155.7	8.39
150	9.52	0.107	54.8	149.3	8.67
160	8.45	0.1085	55.4	141.7	9.03
170	7.34	0.1105	56.3	133.6	9.51
180	6.23	0.112	57.0	124.9	10.1
190	5.13	0.112	57.0	114.8	10.7
200	3.99	0.1105	50.7	104.0	11.5
210	2.91	0.1065	54.3	91.8	12.3
220	1.87	0.100	51.2	78.3	13.3
230	0.91	0.089	45.7	62.5	14.5
234	0.59	0.082	. . . .	. . . .	. . . .
236	0.43	0.077	. . . .	. . . .	. . . .
240	0.15	. . .	. . . .	35.6	. . . .
243.1	0	. . .	. . . .	0	. . .

For it was further shown that the true heat of vaporization, even in the immediate neighborhood of the critical temperature, can be very closely obtained by means of two equations, one proposed by Mills and the other by Dieterici. Values thus obtained, designated Mills and Dieterici, respectively, are given in the tables for comparison, and the constant shown as calculated from them. But one conclusion is possible when the papers cited and the results shown have been studied: *The increase in the value of the constant near the critical temperature is not largely due to errors in the values of the heats of vaporization used.*

Are then the surface tension measurements in error? The surface tensions used were calculated by Ramsay and Shields from the rise of the liquid in a capillary tube by means of the formula

$$5. \qquad \gamma = \tfrac{1}{2}\, r.\, h.\, g.\, (d - D),$$

where r is the radius of the tube, h is the height to which the liquid is raised, g is the gravitation constant, and d and D are the densities of the liquid and its saturated vapor at the temperature of the experiment. Since errors in r and g could not thus affect the result, we have only to consider the probable size of the errors in h and in $d - D$. There seems no good reason to suppose that large and regular errors were made in the determinations of the height of the rise of the liquid in the capillary tube. Regarding the possibility of errors in $d - D$, it is clear that, since d approaches D in value as the critical temperature is approached, errors of measurement of the densities will be greatly multiplied near the critical temperature in their effect upon γ. But the well-known form of the density curves and the law of "rectilinear diameters" aids greatly in smoothing out individual errors of observation. The papers of Ramsay and Shields do not state from what source the densities were obtained, but comparison makes it fairly certain that the measurements for ethyl oxide and water (except the densities for these two substances of the liquid to 100°), methyl and ethyl alcohols, and acetic acid were by Ramsay and Young, for methyl formate and ethyl acetate by Young and Thomas, for benzene, chlorobenzene, and carbon tetrachloride by Young. The measurements of these investigators, as is well known, are exceedingly accurate and would introduce only comparatively small errors in γ. (We would note a misprint in the density of methyl formate, liquid at 140°, 0.7368 for 0.7638, also in accordance with Young's data, carbon tetrachloride vapor at 230° should be 0.1232; benzene at 280° should be 0.1660; and ethyl alcohol at 200° should be 0.5568 for the liquid. The values for acetic acid have been revised by Young, the only changes of significance for our purpose being at 280° where the density of the liquid should be 0.6629 and of the vapor 0.0883; and at 320° for the vapor, which should be 0.2421. These changes will not affect the character of the results shown in the tables.) We conclude therefore *that the sur-*

face tension measurements are fairly accurate and cannot directly cause the variation shown in the constant.

A relatively very large error is introduced in the determination of $d\gamma/dT$. For near the critical temperature $-T\,d\gamma/dT$ becomes very large compared to γ and errors in $d\gamma/dT$ affect the constant almost proportionately. In determining $d\gamma/dT$ we deal with the difference of measurements of γ in themselves nearly equal and subject to some individual error. We would be inclined to think that with any one substance the error introduced into the constant through the uncertainty of the factor $d\gamma/dT$ might be quite sufficient to explain the rise in the value of the constant at the critical temperature. But there seems no reason to suppose that the error thus introduced would always be large and in the same direction, unless there is some undiscovered defect in the determination of the surface tension. Nor is it reasonable to suppose that the consistently recurring decrease, even though it be small, in the value of the constant at low temperatures, is to be attributed to chance errors in the measurements.

The authors therefore conclude *that the variation of the constant in the relation, $E/T\lambda$ = constant, proposed by Whittaker, is not due to the measurements used in testing the relation, but to the fact that the relation is only approximately true.*

With regard to the associated liquids, as was to be expected, the constant makes no pretense of constancy for the alcohols. But contrary to expectation, the constant remains as near a constant for water and acetic acid as it does for the non-associated liquids. We have no idea of the reason for this behavior.

It is seldom that any physical relation holds exactly true throughout a wide range of temperature. It is therefore quite reasonable to study further the relation stated by Whittaker and to seek a possible cause for the same. One of the authors in a paper already cited has discussed theoretically, and carefully tested by means of the extensive series of exact measurements available, the three following equations for the internal heat of vaporization:

$$2.\quad \lambda = \left(T\frac{dP}{dT} - P\right)(V - v) = 0.0_43183\left(T\frac{dP}{dT} - P\right)(V - v) \text{ calories.}$$

$$6.\quad \lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D}) \text{ calories.}$$

$$7.\quad \lambda = CRT\,ln\,\frac{d}{D} = 4.77\,C\,\frac{T}{m}\log\frac{d}{D} \text{ calories.}$$

Equation 2 is the thermodynamical equation already mentioned. In obtaining the constant the pressure is expressed in millimeters of mercury, and v and V are the volumes occupied by a gram of the liquid and of its saturated vapor.

In equation 6 μ' is a constant for any particular non-associated liquid,

d is the density of the liquid, and D is the density of the saturated vapor. The values of μ' for the substances studied in this paper are given in Table XI. The equation was deduced theoretically by Mills from assumptions regarding the molecular attraction and has been extensively studied[1] and would seem to be exactly true for normal non-associated liquids.

In equation 7 C is a constant for any particular substance, having approximately the same value, 1.755, for all normal non-associated liquids, R is the usual gas constant, and d and D represent densities as before. The values for C are given in Table XI. The equation was first proposed as an empirical equation by Dieterici[2] and has been further studied by Richter[3] and by Mills.[4]

Inserting the values of E and λ from equations 1 and 2 in equation 3, we get,

$$8. \qquad \frac{\gamma - T\dfrac{d\gamma}{dT}}{T\left(T\dfrac{dP}{dT} - P\right)(V - v)} = \text{constant},$$

as the form of the relation already studied. Now if it were possible to get the limit of this equation at the critical temperature a further test of its truth could be applied. This does not seem possible with our present knowledge. γ probably falls out and T cancels, leaving

$$\frac{d\gamma}{dT}\Big/\left(T\frac{dP}{dT} - P\right)(V - v)$$

as the indigestible form of the equation. The combination of the equations 1, 2 and 3 under approximate conditions has been studied by Kleeman in the papers cited.

Next combining the relation given in equation 6 with that of Whittaker we obtain, calling the constant of Whittaker's relation k,

$$9. \qquad E = k\mu'T(\sqrt[3]{d} - \sqrt[3]{D}).$$

The values of $k\mu'$ are given in Table XI, though we have as yet been able to draw no conclusion from their product. That the surface energy of a liquid should be proportional to the product of the absolute temperature and the difference of the cube roots of the densities of the liquid and vapor is very suggestive. For it has been shown in the papers by Mills already cited that equation 6 expresses a relation between the molecular attractive forces, and that this relation leads to the conclusion that $\mu'\sqrt[3]{d}$ is the energy necessary to overcome the molecular attraction in pulling the molecules of a liquid apart to an infinite distance. Similarly $\mu' \sqrt[3]{D}$ would represent the energy necessary to pull apart the molecules of a vapor to an infinite distance, the temperature of the vapor remaining constant. Now the so-called liquid surface is really the resultant of two surface layers, the one of the liquid and the other of its vapor, in contact, with oppositely directed forces. Hence it would seem that the total surface energy of a liquid, as usually so-called, can be divided into two parts, one part due to the liquid E_L and the other part due to the vapor over the liquid E_V, the resultant forces being oppositely directed and the surface energy of opposite sign from the standpoint of a surface molecule. We can then write the equations:

---

[1] *J. Phys. Chem*, **6,** 209 (1902); **8,** 383 (1904); **8,** 593 (1904); **9,** 402 (1905); **10,** 1 (1906); **11,** 132 (1907); **11,** 594 (1907); **13,** 512 (1909). THIS JOURNAL, **31,** 1099 (1909).

[2] *Ann. Physik,* **12,** 144 (1903).

[3] "Ueber die innerer Verdampfungswärme," Rostock, 1908.

[4] THIS JOURNAL, **31,** 1099 (1909).

10. $$E_L = K'T\sqrt[3]{d}.$$

11. $$E_V = K'T\sqrt[3]{D}.$$

12. $$E_L - E_V = E = K'T(\sqrt[3]{d} - \sqrt[3]{D}).$$

Perhaps equations 10, 11, and 12 do not express a point of view entirely new so much as they serve merely to add emphasis and give a quantitative expression to a fact already well known,[1] namely, that the nature of the surrounding gas influences the surface tension. It would seem from the suggested equations that perhaps the amount of such influence has been greatly underestimated.

It would seem probable that if equations 10, 11 and 12 are true, the surface tension as usually measured should similarly be capable of division into two parts, one part due to the liquid surface, the other part due to the gaseous surface over the liquid. Such a process of division might result in finding simpler and more accurate relations between the surface tension and other quantities. Search by one of us for the proper modification to be applied to the liquid surface tension as usually measured in order to eliminate the effect of the vapor has apparently met with success, and if a full investigation confirms the results already derived the investigation will shortly be published.

TABLE XI.

	Molecular weight			$10^4E/T\lambda$		
	m	μ'	C	10^4k	$10^4\mu'k$	10^4Ck
Ethyl oxide.......	74.08	103 76	1 724	20 56	2132	3544
Carbon tetrachloride.	153.8	44 01	1 667	38 00	1672	6335
Benzene........ ..	78.05	109 26	1.690	19 42	2122	3282
Chlorobenzene.... ..	112 49	81 66	1 714	21 19	1730	3631
Methyl formate . . .	60 032	119 86	1 706	21.44	2570	3657
Ethyl acetate	88.064	98.88	1.812	20 61	2038	3735
Water.............	18 016	555.1*	..	6 85	3802	....
Acetic acid...........	60 032	....	...	14.74	....	....
Methyl alcohol	32.032	305 0*	...	5.88*	1794	....
Ethyl alcohol	46 048	240 9*	...	7.42*	1787	....

---

[1] See paper by Ramsay and Shields already cited, page 666, and similar determinations by others.

* Not constant.

If the value of λ from equation 7 be used in the equation 3 proposed by Whittaker we have

$$E = kCRT^2 \ln \frac{d}{D}. \tag{13}$$

The value of the product 10^4Ck is given in Table XI, but we can draw no conclusion of interest from the result. Equation 7, as has been shown in the papers cited, is not exactly true at very low vapor pressures for the liquid, but the error is probably not so great as one calorie for any of the non-associated substances over the entire range of temperature covered by the present investigation. The errors introduced by equation 7 are therefore far less than the errors of equation 2 with which it was combined.

Equation 13 is similar to equation 9 in its suggestion of a division of the total surface energy into two parts, one due to the liquid and the other due to the vapor. The resulting equations can be written,

$$E_L = K''RT^2 \ln d, \tag{14}$$

$$E_V = K''RT^2 \ln D, \tag{15}$$

$$E_L - E_V = E = K''RT^2 \ln \frac{d}{D}, \tag{16}$$

where $K'' = Ck$. These relations will also be further studied.

In conclusion, we differ from the arguments and conclusions advanced in the papers by Kleeman already cited at many points, but we would call particular attention to but two things: *First.*—In the investigation of the *inverse fifth power* law of the molecular attraction[1] he uses data from the papers already cited on molecular attraction by Mills. He ignores the fact that in those papers it has been shown that the assumption of the *inverse square* law of the distance gives a consistent agreement with the data over the entire range of temperature, not only for the substances that he investigates but for numerous others. Also when the results within 20° of the critical temperature are left out of consideration Kleeman obtains a consistent decrease of about 25 per cent. in his results at different temperatures. If the attractive force did not vary with the temperature, the greatest allowable variation from the mean to be attributed to the usual errors in the data should be 2 per cent., and we have shown that the *inverse square law* gives results within this limit—and usually far within this limit—for eight substances investigated gave no divergence from the mean greater than 1 per cent.

Second.—To explain the variation he obtains, Kleeman thinks that the force of attraction may diminish with rise of temperature. The papers by Mills as cited find that as regards the molecular attraction all of the evidence disproves this position, and as regards the chemical attraction, the possibility of a change of attraction with temperature was further especially considered in a paper on chemical energy,[1] and no evidence whatever for such a belief was found in the case investigated.

---

[1] *Phil. Mag.*, 19, 795 (1910)

Summary.

1. The relation proposed by Whittaker that "The surface energy of a liquid in contact with its own vapor at any temperature is proportional to the product of the internal latent heat and the (absolute) temperature" has been investigated and the conclusion drawn that the relation is only approximately true.

2. The relation is shown to suggest a division of the so-called surface energy of a liquid into two parts, one part due to the liquid surface and the other to the surface of the vapor over the liquid. Further investigation of this suggestion is promised.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE ADIABATIC DETERMINATION OF HEATS OF SOLUTION OF METALS IN ACIDS.

PART II. THE HEAT OF DILUTION OF THE ACID SOLUTIONS.

BY THEODORE W. RICHARDS, ALLEN W. ROWE AND L. L. BURGESS.

Received July 8, 1910.

Introduction.

An account of a new series of determinations of the heat of solution of five metals in fairly concentrated acids was published in a recent number of THIS JOURNAL.[2] There it was shown that the heats of dilution, both of the acids and of the residual solutions after the reactions had been completed, affect the result much more than has usually been supposed. It was made clear that the actual results of the heats of solution of the metals in fairly concentrated acids must receive large corrections in order that they may all be reduced to the common standard of the heat of solution of the metal in the theoretical amount of acid of the standard dilution $HCl.200H_2O$. The actual attainment in a single experiment of this theoretical result is not possible because the completion of the reaction of the theoretical quantities would require an exceedingly long time, and therefore could not be measured with precision in the calorimeter.

As an example of the correction of the results, the case of zinc may be cited. In a single experiment 7 496 grams of pure zinc were dissolved in 941.4 grams of acid of the concentration $HCl.20H_2O$, and in the process 3461.0 calories of heat were evolved. This amount of zinc is 0.11467 gram atom, and the solution actually in the calorimeter contained 2.372

---

[1] *Trans. Am. Electrochem. Soc.*, 14, 35 (1908).

[2] Richards and Burgess, THIS JOURNAL, 32, 431 (1910).

gram molecules of hydrogen chloride. Accordingly the actual reaction in the calorimeter was as follows:

$$0.11467\ Zn + 2.372\ (HCl.20H_2O) = 0.11467\ H_2 + (0.11467\ ZnCl_2 + 2.143\ HCl + 47.44\ H_2O) + 3461 \text{ calories.}$$

On multiplying this equation by 8.721 in order to find the amount of heat evolved by the solution of 1 gram atom of the metal, the following equation is obtained:

$$Zn + (20.69\ HCl + 414\ H_2O) = H_2 + (ZnCl_2 + 18.69\ HCl + 414\ H_2O)$$
$$(x = 30183 \text{ calories or } 126.8 \text{ kilojoules}).$$

Thus a very large excess of acid was used. The following additional equations (analogous to those already given on page 134 of the article just mentioned) are necessary in order to reduce the result to the more generally useful equation:

$$Zn + 2(HCl.200H_2O) = ZnCl_2\ 400H_2O + H_2 + Q \text{ kilojoules.}$$

In the first place the heat evolved by the dilution of all the hydrochloric acid is needed, in the next place the heat of dilution of all the residual solution, and finally the heat of mixture of dilute solutions of zinc chloride and hydrochloric acid. These are given in order below:

$$20\ 69(HCl + 200H_2O) + 3724H_2O = 20.69(HCl + 200H_2O) + y \text{ kj.} \quad (2)$$

$$(ZnCl_2 + 18.69\ HCl + 414H_2O) + 3724H_2O = (ZnCl_2 + 18.69HCl + 4138H_2O) + z \text{ kj.} \quad (3)$$

$$(ZnCl_2 + 400H_2O) + 18\ 691(HCl + 200H_2O) = (ZnCl_2 + 18.69HCl + 4138H_2O) + q \text{ kj.} \quad (4)$$

From these equations, by simple elimination or cancellation, the desired result is easily found to be as follows:

$$Zn + 2(HCl.200H_2O) = H_2 + ZnCl_2.400H_2O + 126.8 - y + z - q \text{ kj.}$$

Therefore the quantity sought, $Q = 126.8\text{kj.} + (z - y) - q$. It will be shown that the quantity q is zero in all the cases under consideration, hence it is clear that the ideal value for the heat of solution of the metal in dilute acid is to be obtained by adding to the heat of solution in concentrated acid the difference between the heat of dilution of the mixture remaining after the reaction and heat of dilution of all the acid originally taken. The fact that the quantity $(z - y)$ is a difference of similar quantities obtained in precisely the same way greatly increases the ease of determining it accurately, for any systematic errors in y would appear also in z, and hence be eliminated from the result $(z - y)$.

Similar sets of equations with the appropriate concentrations of acid must be used in the cases of aluminium, cadmium, and iron. In the case of magnesium, in which the proper concentration ($HCl.200H_2O$) of hydrochloric acid had been used in the first place, only one of these equations, that corresponding to (1) above, is necessary. Thus, in order to reduce the results given in the preceding paper to the same standard, eleven series of experiments on heat of dilution must be made, in order to determine the quantity y for two strengths of acid, the quantities z and q in four of the cases, and the quantity q in the fifth.

Before beginning the experimental work, two theoretical questions of great importance face the experimenter, namely, first, the question as to the temperature at which these dilutions should be conducted, and, secondly, the further question as to the heat capacity (whether that of the factors or that of the products) which should be used in the calculation of the several heats of dilution. These questions are connected with one another, and may be answered together.

At first it might be supposed that the heat of dilution of the hydrochloric acid should be measured at the initial temperature of the main reaction (namely, about 16°) because this is the only temperature in the process at which the acid solution exists unchanged. This interpretation is nevertheless illusory and erroneous. Although the main reaction of acid on metal takes place over the range from 16 to 20°, the result as calculated from the heat capacity of the factors corresponds to the heat given out by the reaction *conducted isothermally at the final temperature of 20°.*[1]

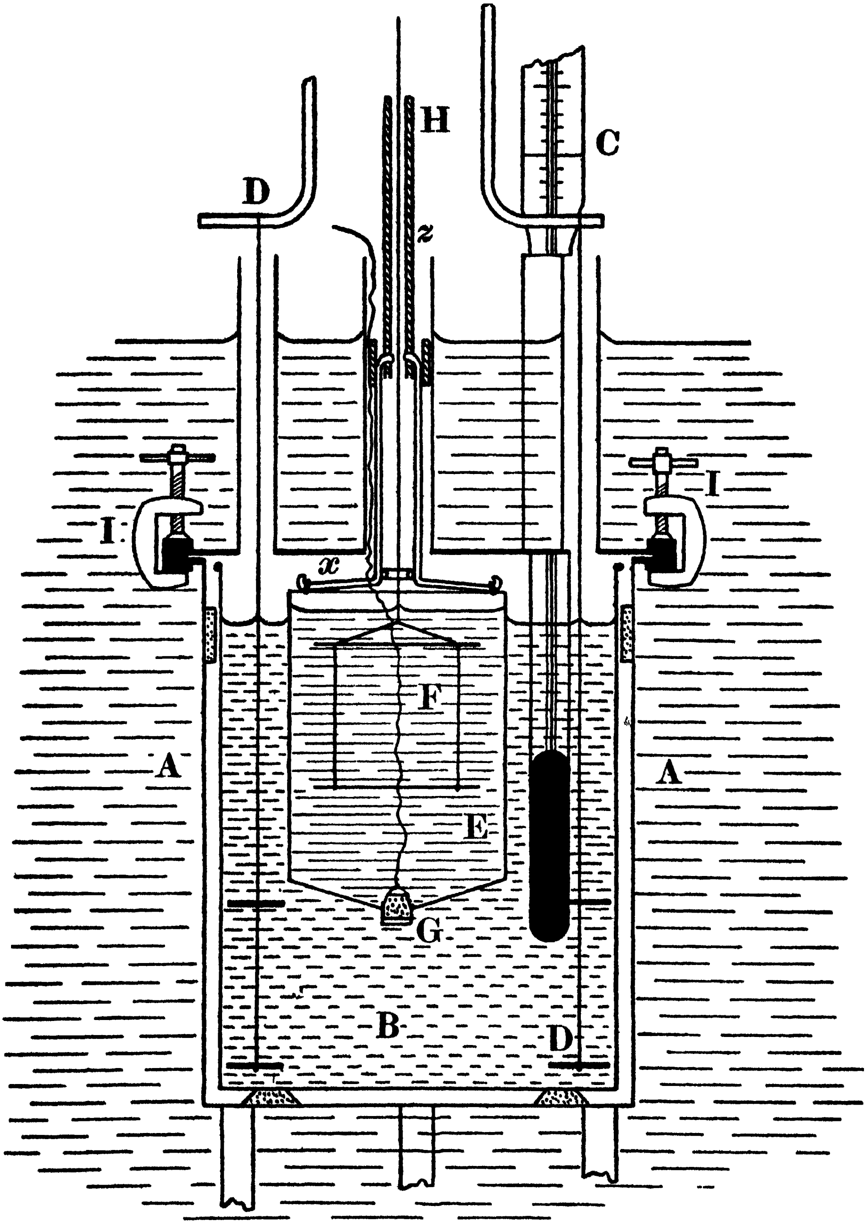
In thermochemical work precision in reasoning is only attained when all the data are reduced to an isothermal basis. Hence it is clear that all the dilutions must be conducted in such a way as to correspond to this same isothermal standard of 20°. This end may be effected in either of two ways: the dilution may be started at 20°, and the heat capacity of the product used in the calculation, or the dilution may be arranged so as to finish at 20° and the heat capacity of the *factors* used in the calculation. The latter method was used, because it was somewhat more convenient. Attention should perhaps be called to the fact that for the sake of ideal consistency, the specific heats used in these calculations should correspond to the small range of a few tenths of a degree just below 20°, and not to the whole range from 16 to 20°. This subtlety, however, may be safely overlooked in the present case, as the slight error which thereby arises in the individual data will appear in all, and will hence be cancelled in the final calculation of the quantity $(z - y)$. Moreover, because in the results to be tabulated, nine-tenths or more of the heat capacity was due to pure water (obviously, the chief factor in the dilution experiments) a large error in the specific heat of the concentrated solution produces very little effect on the result. Accordingly, the specific heats already given for the two acids, $HCl.8.808H_2O$ and HCl $20.00\ H_2O$—namely, 0.7312 and 0.8486—were used in the calculation.

---

[1] Richards, THIS JOURNAL, 25, 209 (1903).

Calorimeter for Dilution Experiments.

For determining the heats of dilution of the acid liquids, that is to say, the parallel quantities y and z, special apparatus was needed. We employed for this purpose a device essentially similar to that used by Rich-



ards, Henderson, and Forbes in a previous investigation.[1] In this apparatus the concentrated solution was enclosed in a receptacle partly immersed beneath the water in the calorimeter; when both liquids had attained exactly the same temperature, the inner vessel was put into connection with the outer, and by suitable stirring the fluids were mixed.

The special form of apparatus used in this case was slightly different from that employed in the previous investigation. It is shown in the accompanying diagram. The inner vessel consisted of a platinum cylinder wholly open at the top, and having a small opening in the bottom. It was suspended on stout platinum wires, connected with thin hard-rubber rods above. The hole in the bottom was stopped by means of a small rubber stopper, the handle of which projected through the cover of the calorimeter. The inner vessel was filled with the solution to be diluted, and a small hand-driven propeller (made by sealing pieces of platinum foil to the sides of a thin-walled glass tube) served to stir it. The calculated amount of water was placed in the outer calorimeter, and the apparatus was adjusted to the position shown in the diagram. The thermometer was a new, very carefully calibrated instrument with degrees 10 centimeters long. When it had attained constancy after a prolonged stirring of both liquids, the plug was pulled out, and the inner platinum vessel lowered until it was entirely immersed in the water, the acid being free to escape both above and below. The liquid in the innner platinum vessel was then easily mixed with the water outside, because the outer stirrer, consisting of two rings of stout platinum foil with a vertical stroke, forced the liquid backwards and forwards through the inner cylinder after the fashion of a pump. The whole calorimeter vessel was enclosed in a larger copper vessel, nickel-plated inside and provided with tubes above for the stirrer, thermometer, and actuating mechanism. This "submarine" apparatus was surrounded by a concentric jacketing vessel, containing dilute alkali to which was added sulphuric acid at such a rate that the outer temperature exactly kept pace with the inner. The heat capacity of all the platinum parts, the rubber stopper, and the thermometer were equivalent to a sum total of 15.37 grams of water. The heat evolved by the stirring apparatus in the inner calorimeter was determined as a part of each experiment. The rate of the motor was such that it was usually sufficient to raise the temperature of the calorimeter at a rate of 0.004° in 10 minutes, the maximum time of the experiment. The correction is duly applied in each case for this extra heat.

There follow the experimental results for the heats of dilution of the two more concentrated solutions of hydrochloric acid. This table explains itself and presents no obscure features. Incidentally it may be remarked that the heat of dilution of $HCl.20H_2O$ at 16°, four degrees lower than that mentioned in the table below, was also determined and found to be not far from seven per cent. less than the values given below. These results, however, do not concern the present investigation, and will be published in another connection.

---

[1] *Proc. Am. Acad.*, 41, 11 (1905). *Z. physik. Chem.*, 52, 560 (1905).

HEAT OF DILUTION OF HYDROCHLORIC ACID AT 25°.

Expt No.	Reaction measured	Temp of experiment	Corrected rise of temperature.	Heat capacity in Cal./t° units.	Average energy change, Cal.	Energy change for 1 mol. HCl in large Calories.
1	130 0 grams HCl	19.88	0.152			
2	20.H_2O + 1062 5	19 93	0 153	1188.1	181.5	0.556
3	grams H_2O	19.93	0 153			
4		19 93	0 153			
5	60.0 grams HCl	19 8	0.365			
6	8.8H_2O + 1059	19.8	0.366	1118 3	408.2	1 330
7	grams H_2O	19.8	0.366			
8		19.8	0.366			

The numbers given in the last column of the foregoing table indicate that when to $HCl.20H_2O$ is added $180H_2O$, 0.556 Calories of heat are evolved at 20°, and that when $HCl.8\ 81H_2O$ is diluted with $191.2H_2O$, 1.330 Calories are evolved. For use in calculating the value y in several equations, these numbers must of course be multiplied by the number of moles of hydrochloric acid concerned in the actual reaction. For instance, in the case of zinc one gram atom of the metal was dissolved in a solution containing 20 69 moles of $HCl.20H_2O$. Therefore y in this case equals 0.556 × 20 69 or 11.5 Calories. Other factors are obviously necessary in the other cases; these factors will be named later.

The preliminary experiments with the solutions left in the calorimeter after the metals had been dissolved in the acid showed that considerable change in the heat of dilution is caused by the presence of the metal instead of hydrogen, which it had displaced. Thus the heat of dilution of the solution containing zinc was found to be over 0 08° more than the hydrochloric acid and the aluminium a few thousandths of a degree. On the other hand, the heat of dilution of the solution containing cadmium was less than that of the hydrochloric acid from which it was made by about 0.02° and the ferrous chloride solution remaining from the experiment with iron showed a very slight difference indeed, when compared to the pure acid. These results show that the heats of dilution may be a very serious factor in the result, and that they must therefore be determined with the greatest possible care. The next table records these very careful experiments, giving the heats of dilution of the mixed solutions remaining after the reaction, solutions which still contained a large excess of hydrochloric acid, but also a small amount of the dissolved chloride of the metal. These determinations were made in precisely the same way, as nearly as possible, as the experiments with pure hydrochloric acid. The same part of the thermometer was used, so that undetected errors in calibration, if present, would be automatically cancelled from the final result.

The dilution of the ferrous chloride solution presented some difficulty, owing to its tendency to oxidize. Obviously, results obtained with a solution which had oxidized either before or during the dilution experiment would be worthless. To prevent the solution from oxidizing before use, it was prepared in a flask connected with a hydrogen generator and fitted with a siphon and a delivery tube. In this way an atmosphere of hydrogen was maintained above the solution, and no oxidation could occur. The end of the siphon was kept under toluene, and the first portion discharged always rejected. During the experiment the surface of the liquids, both in the platinum container and in the calorimeter can, were covered with a layer of toluene, which sufficiently prevented access of air during the brief time of the experiment. The water used was, of course, boiled to free it from dissolved air. The toluene was first weighed into the inner platinum vessel and then the end of the siphon, which was drawn out to a long capillary, was inserted below the surface of the toluene and the ferrous solution allowed to run. When carried out in this fashion, the solution contained only the merest trace of ferric salt previous to the mixing, and after the mixing had been accomplished there was no appreciable increase, as estimated by colorimetric comparison, with sulphocyanate.

In order to calculate the heat of dilution the heat capacity of the two liquids being mixed must be known. One of these is pure water, the other a solution of hydrochloric acid containing a small amount of metal. From the results of Marignac it seemed probable that the substitution of the small amount of metal for some of the hydrogen in the acid would not have a very great effect upon the heat capacity of a given quantity of the acid. From his results it is apparent, for example, that the conversion of $2(HCl.25H_2O)$ into $SrCl_2.50H_2O$ causes a change in heat capacity of only about 1 per cent. Data in other cases are lacking, but this case may be taken as typical.[1] In order to make assurance doubly sure, however, the case of zinc (which gave the most divergent results) was tested with great care. 636 grams of $HCl.20H_2O$ were treated with about 5 grams of zinc. When the solution was complete, the specific heat of the resulting mixture was found by two very concordant results to be 0.8575. Hence the heat capacity of the total amount taken was $641 \times 0.8575 = 549$ "calorie units." The acid from which the solution was made had a heat capacity of 540. Thus there is a gain of heat capacity, owing to the substitution of zinc for hydrogen, of less than 2 per cent. Clearly this is a change too small to have any serious effect upon the results of the heat of dilution; for the greater part of the heat capacity in dilution experiments is due to the water and not to the much smaller bulk of acid solution. An error of 2 per cent. in the heat capacity of the zinc solution would cause only 0.2 per cent. in the total heat capacity—a range of accuracy beyond one's ability to read the thermometers concerned in determining the heat of dilution. Because the most divergent case was that of zinc, it seems clear that no important error would be introduced by assuming that the heat capacity of the solution in all the other cases is equal to that of the hydrochloric acid from which the solutions were made. In yet more accurate work this point would demand consideration.

---

[1] *Ann. chim. phys.*, [5] 8, 410 (1876).

A table containing four series of experiments wth these residual liquids is given below:

HEAT OF DILUTION OF FINAL SOLUTIONS.

Expt No	Reaction measured.	Initial temperature of experiment.	Corrected rise of temperature	Heat capacity in Cal./t° units.	Energy change, Calories	Energy change for 1 gram atom of chlorine in large Calories.
11	125.0 grams of zinc soln + 1013.7 grams of water	19.95	0.238°	1136	0.2715	0.868
12		19.94	0.238			
13		19.99	0.240			
14		19.94	0.239			
15		19.96	0.240			
16	125 grams aluminium soln. + 1020.9 grams water	19.94	0.156	1142	0.1784	0.567
17		19.92	0.156			
18		19.95	0.156			
19		19.94	0.156			
20		19.96	0.157			
21	60 grams cadmium soln. + 1043.4 grams water	19.90	0.346	1102	0.3824	1.262
22		11.94	0.348			
23		19.93	0.348			
24		19.93	0.347			
25		19.94	0.348			
26	60 grams ferrous soln. + 1049.7 grams water	19.94	0.368	1109	0.4081	1.339
27		19.93	0.369			
28		19.94	0.368			
29		19.94	0.367			
30		19.94	0.367			

The data given in the last column of this table are used for the calculation of the quantity z, by multiplication with the appropriate factor. In the case of zinc, this factor is, as before, 20.69, because 20.69 molecules of hydrochloric acid were present for each atom of zinc. The other factors are given below in the next table.

The marked differences between the heats of dilution of the solutions containing small amounts of zinc and aluminium, but otherwise alike, is very interesting. The correspondence with the preliminary results is very close.

It is not necessary to give the full details of the careful experiments indicating the complete absence of heat of mixture of $(^1/_n\mathrm{MCl}_n)$ $200\mathrm{H_2O}$ with an excess of $\mathrm{HCl.200H_2O}$. Ten experiments of this kind were made, two with each of the chlorides of zinc, aluminium, magnesium, cadmium, and iron in place of MCl_n. Exact weighing was not necessary in these cases because a slight excess of one or the other reagent would have a vanishingly small effect, since the total change to be measured was found to be imperceptible. In no case was a perceptible evolution of heat observed in these reactions. Hence the quantity q in the previous equations became 0 in each case, as has been already stated.

Calculation of Final Results.

The various data concerning dilution may now be applied to the heats of solution of the metals in concentrated acids, thus computing the theoretical value of the heat which the reactions would evolve in each case, provided that the metal were dissolved in just enough $\mathrm{HCl} + 200\mathrm{H_2O}$ to effect its complete solution, giving a product free from excess of acid. In order to accomplish this, there must be in each case subtracted from the value of the heat of solution actually observed for a gram atom of metal, the heat of dilution of the hydrochloric acid employed under the experimental conditions to act upon a gram atom of metal; and there must be added to the result the heat of dilution of the corresponding quantity of residual solution. The following table indicates the number of moles of acid corresponding to a gram atom of metal, the data being taken from the record of the experiments already given in the previous paper:

MOLECULAR PROPORTIONS OF ACID AND METAL.

	Weight of metal.	Atomic weight.	Fraction of gram atom present.	Gram mols. of acid present.	Gram mols. of acid for each gram atom of metal
Zinc	7.496	65.37	0.11467	2.372	20.69
Aluminium	0.747	27.1	0.02756	2.372	86.06
Magnesium	0.849	24.32	0.03492	...	...
Cadmium	14.983	112.32	0.13328	5.038	37.80
Iron	9.000	55.85	0.16114	5.037	31.26

The values given in the final column of this table are the factors needed in order to calculate the values of y and z from the values given in the last columns of the two preceding tables respectively.

The values for y and z calculated in this way from these data for each of the four metals, zinc, aluminium, iron, and cadmium, are given in the following table: The table contains the values for x, the heat of solution of the metal in the excess of concentrated acid (repeated from the previous paper), and also the final result sought, $x + (z - y)$:

Metal concerned.	x in Calories.	y in Calories.	z in Calories.	$x + (z - y)$ in Calories.	Thomsen's values.
Zinc................	30.18	11.50	17.94	36.6	34.2
Aluminium...	126.0	47.81	48.8	127.0	115.0
Magnesium...	110.15	0	0	110.15	108.7
Cadmium	19.77	50.27	47.70	17.2	17.6
Iron....	20.55	41.57	41.85	20.8	21.3

Thus the new values for the heats of reaction sought are as follows:

$Zn + 2HCl\,aq = ZnCl_2\,aq + H_2 + 36.6$ Cal. or 153.1 kilojoules.

$Al + 3HCl\,aq = AlCl_3\,aq + 3/2H_2 + 127.0$ Cal. or 531 kilojoules.

$Mg + 2HCl\,aq = MgCl_2\,aq + H_2 + 110.2$ Cal. or 460.6 kilojoules.

$Cd + 2HCl\,aq = CdCl_2\,aq + H_2 + 17.2$ Cal or 71.9 kilojoules.

$Fe + 2HCl\,aq = FeCl_2\,aq + H_2 + 20.8$ Cal. or 87.0 kilojoules.

The comparison of the new results with Thomsen's values given in the last column shows that the new results differ in some cases considerably from the old value. These differences are to be explained partly by the defect in Rumford's method of correcting for cooling, as used by Thomsen, and partly by his having omitted to add to his results the excess of the heat of dilution of the product over that of the pure acid solution.

It is apparent that the present results are not all equally accurate. In the case of magnesium the result is obtained directly without the necessity of applying any correction for heat of dilution. It is therefore decidedly more certain than the others. In the case of zinc the individual values of the quantities x and y are not large, and supposing these values to be known within one per cent., the error of the final result probably is not more than 0.15 Calorie, or half of 1 per cent. In the case of aluminium the values y and z are larger in actual magnitude, but not larger in proportion to x, therefore the probable percentage error is about the same. In the case of cadmium and iron, the percentage of accuracy of the determination of y and z is greater because the change of temperature involved is greater, but the very large magnitude of each of these quantities (distinctly larger than that of the main reaction) more than neutralizes this advantage.

One favorable circumstance already alluded to mitigates considerably the damaging effect of these difficulties, namely, the fact that y and z are always opposite in sign and nearly equal in magnitude. Because they were observed in precisely the same way under almost similar conditions, it is reasonable to suppose that the same error, if any, applies to both, and that therefore the error would be eliminated.

In order to obtain better results, it would be necessary either to dissolve the metal in a much smaller quantity of less concentrated acid, so that the values y and z should be smaller, or else to observe with greater accuracy than was possible with any means of thermometric measurement at our disposal the heats of dilution of the several solutions. The purity of the metals used preventing the employment of a less concentrated acid because of their slow rate of solution, the latter alternative is perhaps the easier of the two. It is hoped in the near future that the experience gained in this research may be applied in a more complete manner. In the meantime the results here given must be looked upon as merely preliminary. At least it is hoped that the present papers have succeeded in putting the subject of the heats of solution of metals upon a sound scientific basis, to which the future can add nothing more than perfection of detail.

In conclusion, it is a pleasure to express our indebtedness to the generosity of the Carnegie Institution of Washington for pecuniary assistance.

Summary.

There follows in a few words a statement of the outcome of this paper:

1. The heats of dilution of the acids $HCl.20H_2O$ and $HCl.8.808$ to $HCl.200H_2O$ were determined. The results are 0.556 and 1.330 Calories (2.32 and 5.56 kilojoules) respectively.
2. The heats of dilution of the several products obtained by dissolving four metals in excess of concentrated acid were determined. The substitution of salt for acid was found, especially in the cases of zinc and cadmium, to affect seriously the heat of dilution.
3. From these data the heats of solution of a gram atom of the several metals in exactly the theoretical quantity of $HCl.200H_2O$ have been calculated as follows:

THE HEAT OF REACTION OF METAL ON $HCl.200H_2O$ CALCULATED FOR 1 GRAM ATOM OF METAL.

Metal.	Heat of reaction in 18° Calories.	Heat of reaction in Kilojoules.
Zinc	36 6	153 1
Aluminium	127.0	531.0
Magnesium	110.2	460.6
Cadmium	17.2	71.9
Iron	20.8	87.0

[CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

THE INCONSTANCY OF THE SOLUBILITY PRODUCT.[1]

BY ARTHUR E. HILL.

Received July 11, 1910.

The various assumptions made by Nernst[2] and A. A. Noyes[3] in their earlier investigations on the solubility of electrolytes have been subjected to careful scrutiny by their many successors in this field of work. As in the case of most pioneer work done in theoretical chemistry, it has here developed that many of the assumptions have been too broad, and that they must be subjected to considerable modification if they are to be adopted as a basis for the quantitative study of solutions of electrolytes. Of these original assumptions, two have been almost entirely displaced from the minds of chemists. The belief in the constancy of the concentration of the undissociated molecules of a dissolved electrolyte in equilibrium with its solid phase was shown to be untenable by the experimental work of Arrhenius,[1] which proved beyond question of doubt that this concentration diminishes as the total concentration of salts present is increased. In a like manner, the simplifying assumption that the degree of dissociation is independent of the presence of other electrolytes can no longer be made against the experimental evidence which has been accumulated by Arrhenius,[2] MacGregor, McIntosh, Archibald and McKay,[3] and most recently by Sherrill,[4] all of which makes it reasonably certain that the total concentration of electrolytes present is here also a determining factor.

---

[1] Presented before the New York Section of the American Chemical Society, June 10, 1910.

[2] *Z. physik. Chem.*, 4, 372 (1889).

[3] *Ibid.*, 6, 241 and subsequent papers.

Of these early assumptions, that of the constancy of the solubility product seems to be the one from which there has been least dissent. It is incorporated in the majority of our elementary text-books as a convenient help in the explanation of solubility relations, and has not lacked advocates even within recent years. Stieglitz[5] has recalculated the experiments of Arrhenius, and finds that by assuming the degree of dissociation to be in accordance with Arrhenius' isohydric principle, it is possible to find a satisfactory constancy for the solubility product, which, he maintains, we may well consider for the present to be an approximate empirical principle, in the absence of theoretical grounds upon which it may stand. Such a theoretical basis Washburn[6] considers to exist in the laws of osmotic pressure, developed with reference to "normal solutes," and "ideal solutions."

Direct experimental proof of the constancy of this value can hardly be looked for, since the concentration of the ions of the solute cannot be directly measured, the calculations based on solubility experiments are complicated by the necessity of making other assumptions as to the state of dissociation and the concentration of undissociated molecules. On the other hand, there already exists, in the solubility experiments of

---

[1] *Z. physik. Chem.*, 31, 224 (1899).

[2] *Ibid.*, 2, 284 (1888); 31, 218 (1899).

[3] *Trans. Nova Scot. Inst. Sci.*, 9–10 (1895–1899).

[4] THIS JOURNAL, 32, 741 (1910).

[5] *Ibid.*, 30, 946 (1908).

[6] *Ibid.*, 32, 487 (1910); 32, 669 (1910).

Cameron[1] and of Hill and Simmons,[2] good reason for the belief that the product of the ions diminishes in value with increase in total concentration of electrolytes. Cameron noted that the solubility of gypsum was increased by addition of sodium chloride up to a certain concentration, beyond which it suffered a decrease; the same phenomenon was found to occur when silver sulphate was acted on by nitric acid solutions.[2] In both these cases, we should expect a continuous increase in solubility, due to the formation of new compounds by chemical interaction. This factor would be opposed by a small decrease in the amount of undissociated salt present, as Arrhenius'[3] experiments clearly prove. This latter factor, however, could not be expected to counterbalance the increase caused by chemical action, since the quantity of undissociated salt is practically negligible in the case of highly dissociated substances such as gypsum and silver sulphate. In order, therefore, to account for the diminution in total solubility, we must assume that the ions of the solute have been lessened in concentration, and that the solubility product accordingly has been diminished in value.

The preceding experiments do not permit any calculations as to the value of the solubility product without the use of the other complicating assumptions. In the belief, however, that the qualitative discussion above was correct in principle, other experiments have been conducted in which, without the addition of any common ion, the solubility of certain salts has been so diminished in the presence of other electrolytes as to prove conclusively, without the introduction of assumptions as to the degree of dissociation or the concentration of undissociated salt, that the solubility product is not a constant, but diminishes in value in the presence of other electrolytes.

In selecting material for the experiments, such pairs of electrolytes were chosen as would be expected to show least chemical interaction, so that the increased solubility due to this action might cease to be the determining factor at a low concentration. Thallous chloride, a salt of a strong acid, was used with acetic acid as the second electrolyte; since the solubility of this salt is not greatly increased even by nitric acid,[4] it was to be expected that the weaker acetic acid would have but little effect in this direction. Tetramethylammonium iodide and potassium hydroxide were taken as the second pair. When each of these pairs was tested, it developed that under no conditions was an increase in solubility of the salt to be noted, while the decrease became clearly marked upon the addition of very moderate amounts of the second electrolyte.

---

[1] *J. Physic. Chem.*, 5, 556 (1910).

[2] THIS JOURNAL, 31, 821 (1909). *Z. physik. Chem.*, 67, 594 (1909).

[3] *Loc. cit.*

[4] Hill and Simmons, *Loc. cit.*

Experimental Part.

The thallous chloride used was prepared from metallic thallium and recrystallized from water. Analyses of the pure compound gave the chlorine content as 14 79 and 14.75 per cent.; calculated, 14.80. The acetic acid was Kahlbaum's c. p. preparation, whose strength was determined by titration against a standard potassium hydroxide solution; the ultimate standard was gravimetrically analyzed hydrochloric acid. The solubility equilibrium was approached from supersaturation and undersaturation. Stirring of the samples for eight hours proved to be sufficient. After equilibrium had been reached, samples were pipetted out and analyzed for their chloride content by Volhard's method, filtering off the silver chloride[1] in each case. In experiments (8) and (9), in which the chloride content was low, gravimetric analyses were made. The specific gravity of the acetic acid solution at the temperature of standardization and that of the saturated solution at 25° were determined by direct weighing of measured volumes.

TABLE I.—SOLUBILITY OF TlCl IN $HC_2H_3O_2$ at 25°.

	Normality of $HC_2H_3O_2$.	Spec. grav. of $HC_2H_3O_2$ at room temp.	Spec. grav. of solution at 25°.	Equivalents TlCl per liter.	Mean solubility per liter.
1	0 000	....	...	0 01628 U 0.01630 S	0.01629
2.	0.5134	0.9996	1 0014	0 01573 U 0.01589 S	0.01580
3.	1 013	1 0010	1 0043	0 01485 U 0 01505 S	0 01495
4 ...	2.016	1 0104	1 0114	0.01319 U 0.01323 S	0 01321
5.	4.180	1 0238	1 0323	0 009938 U 0.009952 S	0.009945
6	8 130	1 0495	1 0550	0 005385 U 0 005413 S	0 005399
7	11 49	1.0623	1 0599	0 002573 U 0 002615 S	0 002594
8............	14.31	1 0657	1 0643	0.001221 U&S	0 001221
9	16.01	1.0667	1 0667	0 000478 U&S	0 000478

The tetramethylammonium iodide used for the second set of experiments was a preparation of Kahlbaum's which was recrystallized from water. Analysis by Volhard's method gave the following figures for iodide content: found, 63.08 and 63 38 per cent.; calculated, 63.13. The potassium hydroxide was freed from carbonates by agitating a concentrated solution with slaked lime; when siphoned off and tested, it was found to be free from calcium. The alkali solutions were made up from this stock solution and titrated against a gravimetrically analyzed hydrochloric acid. Specific gravity and solubility determinations were made as in the case of the thallous chloride, the iodides being determined by the method of Volhard.

---

[1] Rosanoff and Hill, THIS JOURNAL, 29, 269 (1907).

TABLE II.—SOLUBILITY OF $(CH_3)_4NI$ IN KOH AT 25°.

	Normality of KOH.	Spec. grav. of KOH at room temp.	Spec. grav. of solution at 25° C.	Grams $(CH_3)_4NI$ per liter.	Equivalents $(CH_3)_4NI$ per liter
1	0.000	.....	1.0163	53.67 U 53.74 S	0 2671
2	0 250	1.0107	1.0268	51.51 U 51.24 S	0.2556
3	0.5325	1.0264	1.0408	47.66 U 47.93 S	0.2377
4	0 9899	1.0474	1 0601	41.81 U 41.98 S	0.2084
5	2 0743	1 0955	1 1048	28.74 U 29.03 S	0 1437
6	8 2962	1.3450	1.3435	3.022 U 2.909 S	0 01475

The solubility of the salt in water is found to be about one per cent. higher than the value which Walden[1] obtained in the case of an equilibrium approached from undersaturation. Walden's figure where the approach was made from the direction of supersaturation (58 9 grams per liter) shows that a true equilibrium was not attained in his experiment.

Determinations of the conductivity of tetramethylammonium iodide were made for use in the calculations of this paper. A dip cell was used for the measurements, the capacity being determined by means of $N/50$ potassium chloride solution, whose conductivity was taken as 0.002768. The water used in the dilutions had a conductivity of 0.0000029. Experiments were conducted with a saturated solution and with the customary dilutions from $N/8$ to $N/1024$.

TABLE III.—CONDUCTIVITY OF $(CH_3)_4NI$ AT 25° (±0 03°).

	Volume.	Equivalent conductivity.
1	3.74	81.20
2	8.0	88.86
3	16.0	96.54
4	32.0	103.4
5	64.0	109.3
6	128.0	113.9
7	256.0	118.2
8	512.0	121.8
9	1024.0	123.8
—	∞	(129.2)

The value of the equivalent conductivity at infinite dilution was found by extrapolation to zero concentration from the results of experiments 5 to 9, following the method of A. A. Noyes.[1]

---

[1] *Z. physik. Chem.*, 55, 708 (1906).

The limiting value 129.2 is much higher than that which would be found by taking for the migration numbers the accepted value 76.8 for iodide ion and for the tetramethylammonium ion 46 5 as calculated by Bredig[2] from conductivity measurements of the chloride. This value for the tetramethylammonium ion is surely several units too low, as appears when it is used to calculate the dissociation of tetramethylammonium hydroxide from Bredig's measurements;[3] at a dilution of 256, the base appears to have a conductivity corresponding to more than complete dissociation. If the migration number is taken from the above measurements as 52 4, the base is seen to possess only the extent of dissociation common to strong electrolytes, and the anomaly disappears.

Discussion of Results.

It has been shown that a diminution in solubility such as appears in Tables II and III gives strong qualitative indication that the value of the solubility product has also diminished. The case is capable of quantitative treatment where the decrease goes far enough. If in the case of the double decomposition

$$\underset{a}{\mathrm{AB}} + \underset{b}{\mathrm{CD}} \rightleftarrows \underset{c}{\mathrm{AD}} + \underset{d}{\mathrm{CB}},$$

we use the capital letters to indicate concentrations of free ions and the small letters to indicate concentrations of undissociated molecules, we can express the total solubility m of the compound AB in two ways:

$$(1)\ m = \mathrm{A} + a + c;$$

$$(2)\ m = \mathrm{B} + a + d.$$

If we assume the solubility product to have a constant value, we have

$$(3)\ \mathrm{A} \times \mathrm{B} = \mathrm{K}.$$

Multiplying (1) by (2) and extracting the square root, we find

$$(4)\ m = \sqrt{\mathrm{A} \times \mathrm{B}} + \mathrm{X},$$

where X is used to indicate the various other terms, all of which must have a positive value, since a, b, c and d are positive numbers. Substituting from (3), we obtain

$$(5)\ m = \sqrt{\mathrm{K}} + \mathrm{X},$$

which indicates that, on the assumption of the constancy of the solubility product, the total solubility could never be less than the value $\sqrt{\mathrm{K}}$. A value of m less than $\sqrt{\mathrm{K}}$ proves therefore an error in the assumptions of equations 1, 2, or 3. Equations 1 and 2 express the fundamental assumption of the dissociation theory, that the substances present exist as ions and as undissociated molecules; unless we are prepared to deny this, we must grant that a value of m less than $\sqrt{K}$ constitutes rigorous proof that the value of the solubility product has decreased.

---

[1] *Report of the Carnegie Inst.*, 63, 50. See also the paper of Johnston, THIS JOURNAL, 31, 1010 (1910). The value of the exponent n for this salt was found to be 1.48.

[2] *Z. physik. Chem.*, 13, 228 (1894) Bredig's numbers have been multiplied by 1.067.

[3] *Ibid.*, p. 299.

In the following tables the values of m have been arranged with reference to the concentration of other electrolytes present; the values of the solubility product have been calculated for each salt. The solubilities have been calculated with reference to the volume of the solution and to the weight of water present, so that the meaning of the term concentration shall not be in question:

TABLE IV.—SOLUBILITY OF TlCl IN $HC_2H_3O_2$.

Volumetric normality of $HC_2H_3O_2$.	Equivalents TlCl per liter of solution.	Equivalents TlCl per 1000 gms. of H_2O.
0.00	0.01629	0.01634
0.5134	0.01580	0.01628
1.013	0.01495	0.01585
2.016	0.01321*	0.01484*
4.180	0.009945	0.01273
8.130	0.005399	0.00952
11.49	0.002590	0.00792
14.31	0.001221	0.00595
16.01	0.000478	0.00453
	$\sqrt{K}$ = 0.01486[1]	$\sqrt{K}$ = 0.01490

TABLE V.—SOLUBILITY OF $(CH_3)_4NI$ IN KOH.

Volumetric normality of KOH.	Equivalents $(CH_3)_4NI$ per liter of solution.	Equivalents $(CH_3)_4NI$ per 1000 gms. of H_2O.
0.000	0.2671	0.2774
0.250	0.2556	0.2657
0.5325	0.2377	0.2466
0.9899	0.2084	0.2162
2.0743	0.1437*	0.1491*
8.2962	0.01475	0.01683
	$\sqrt{K}$ = 0.1678[2]	$\sqrt{K}$ = 0.1743

It appears in the foregoing tables that the point at which m is found to be less than $\sqrt{K}$ occurs where the solution is at a concentration between normal and twice normal with respect to the second electrolyte. When this latter concentration is increased sufficiently, the solubility is decreased to a value of entirely different magnitude from that in pure water. We are left, therefore, no alternative but to dismiss our belief in the constancy of the solubility product, together with the other early assumptions of the theory of solutions, and to be satisfied for the present with the purely qualitative statement that the solubility product shows a diminishing value with increased concentration of other electrolytes.

---

[1] Calculated from the conductivity measurements of Goodwin, *Z. physik. Chem.*, 13, 608 (1894).

[2] Calculated from the conductivity measurements of Table III.

Conclusion.

The results of the foregoing paper may be summarized as follows:

(1) Determinations have been made of the solubility of thallous chloride in acetic acid solutions of varying concentrations, and of tetramethylammonium iodide in potassium hydroxide solutions of varying concentrations.

(2) The electrical conductivity of tetramethylammonium iodide has been measured.

(3) The solubility product has been shown to have a value which diminishes with increase in the total concentration of electrolytes present.

I am indebted to Mr. George Barmeyer and to Mr. Charles E. Roake for the solubility determinations of Tables I and II.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 54.]

A VOLUMETRIC METHOD OF DETERMINING IODIDE IN THE PRESENCE OF CHLORIDE, BROMIDE, OR FREE IODINE.

BY W. C. BRAY AND G. M. J. MACKAY.

Received July 25, 1910.

The method here described of determining iodide depends upon its oxidation to iodine in acid solution by means of potassium permanganate, the removal of the liberated iodine from the aqueous phase by carbon tetrachloride, and the titration of this iodine with a standard sodium thiosulphate solution. When the iodide contains free iodine dissolved in it this titration gives the total iodine present in solution; the dissolved iodine is determined by direct titration of the original solution with thiosulphate, and the difference between the two results gives the iodine present as iodide.

This method was suggested and used by Sammet,[1] but he gave no specific directions and no indication of its accuracy. A similar method was developed long ago by Fresenius,[2] in which carbon disulphide took the place of carbon tetrachloride, excess of nitrous acid was used instead of an equivalent amount of permanganate, and the nitrous acid in contact with the carbon disulphide was removed by repeated decantations with water. Information with regard to the accuracy of this method appears to be lacking, but it is doubtful if it would have, even if modified, any advantages over the present method.

The possibility of determining iodide in the presence of chloride or

[1] Sammet, *Z. physik. Chem.*, 53, 684 (1905).

[2] Fresenius, *Quant. Anal. 4th reprint* (1900) of 6th edit. (1875), page 482.

bromide depends upon the extremely rapid rate, even in dilute solutions, of the reaction

$$5I^- + MnO_4^- + 8H^+ = 2\tfrac{1}{2}I_2 + Mn^{++} + 4H_2O,$$

and the relatively slow rates of the corresponding reactions with chloride or bromide. The reaction with chloride is so slow that there is no appreciable liberation of chlorine, even in a moderately concentrated sulphuric acid solution. In the case of bromine, however, in order to prevent the rapid liberation of bromide, it is necessary to keep the concentration of bromide and of sulphuric acid small, and to add only a slight excess of permanganate. It will be seen later that none of these precautions introduces any difficulty.

This plan of regulating the rate of reaction between halides and permanganate by means of the hydrogen ion concentration has already been used in a well-known method of detecting the halides in the presence of each other,[1] which was developed by Jannasch and Küster.[2] In this process the halogens are expelled successively from a boiling solution: iodine from a solution containing acetic acid and sodium acetate, bromine from a solution containing acetic acid and a little sulphuric acid, and chlorine from a concentrated sulphuric acid solution. The advantages in our quantitative method of working at room temperature and collecting the liberated iodine in another solvent are obvious. But in this case it was found by trial that dilute sulphuric acid must be used, instead of acetic acid, in order to prevent the formation of manganese dioxide, which interferes with the removal of the CCl_4 phase. Since the liberation of bromine cannot, therefore, be prevented by cutting down the hydrogen ion concentration to a very small value, it is important, as mentioned above, to avoid an excess of permanganate.

The addition of permanganate may be regarded as a titration; the "end point" described below in the procedure is easily determined and it is not difficult to avoid an excess of permanganate. This is possible because a solution of potassium iodide and carbon tetrachloride are both much better solvents for iodine than is pure water, so that, as the potassium iodide concentration becomes smaller, a larger proportion of the iodine passes into the carbon tetrachloride phase, and finally a colorless aqueous layer may be obtained.

The only sources of error in this method appear to be those which might arise from the addition of potassium permanganate in excess. If bromide is present, some bromine may be liberated. Also the addition of potassium permanganate in excess while considerable iodine is still present would result in the permanent formation of some iodic acid, the iodine of which would not be removed by the carbon tetrachloride. The temporary formation of bromine or iodic acid during the earlier part of the operation does not, of course, introduce an error, for each reacts with the iodide still present, forming iodine. Although these errors may be easily avoided, it has seemed worth while to add a supplementary treatment with sulphurous acid by means of which the loss of an analysis may be avoided even if too much permanganate has been added.

---

[1] Boettger, *Qualitative Analysis*, 2nd edit., page 387.

[2] Jannasch and Küster, *Z physik. Chem.*, **28**, 377 (1899).

Method of Analysis.

The following *materials* are required:

A glass-stoppered separating funnel of about 250 cc. capacity in which to carry out the oxidation of the iodide. The delivery tube should be cut off short and ground at an angle in order to facilitate washing after the discharge of the carbon tetrachloride solution of iodine.

A standard sodium thiosulphate solution, say 0.1 or 0.2 normal.

A potassium permanganate solution of about the same strength.

A freshly prepared 10 per cent. potassium iodide solution free from iodate.

Carbon tetrachloride free from oxidizing or reducting agents. A liter of carbon tetrachloride may be conveniently purified for use in these analyses by treating with iodine and dilute sulphuric acid for a few hours, shaking the mixture at intervals. The CCl_4 is drawn off from the acid solution by means of a large separating funnel decolorized by shaking with a neutral sodium thiosulphate solution, and washed thoroughly by shaking with fresh portions of water.

Procedure.—Introduce into the separating funnel 25 to 30 cc. of carbon tetrachloride, 3 to 15 cc. sulphuric acid[1] (sp. gr. 1.20), and a definite amount of the potassium iodide solution to be analyzed. If bromide may be present, do not use more than 5 cc. of sulphuric acid and add 75 to 100 cc. water.

Add the permanganate solution from a burette, at the same time rotating the mixture, until the aqueous layer becomes very dark colored due to the liberated iodine; place the stopper in the separating funnel, shake vigorously, and let stand for at least half a minute. Carefully run the carbon tetrachloride solution of iodine into a glass stoppered flask containing about 25 cc. of 10 per cent. potassium iodide solution[2] and a few drops of acetic acid. Add a fresh portion of carbon tetrachloride and repeat the process until the aqueous layer is colorless.

As this stage is approached, add the permanganate solution drop by drop and shake the mixture after each addition. The decolorization of the permanganate and the liberation of iodine when the drop enters the solution can be easily observed. When the water layer appears colorless, withdraw as much as possible of the iodine by using successive small portions of carbon tetrachloride, add a drop of the permanganate, shake the mixture, and note the color of the aqueous and carbon tetrachloride layers. The end point has been reached (1) if the aqueous solution is pink colored owing to the presence of permanganate, and (2) if the carbon tetrachloride fails to show the pink color due to the presence of iodine.[1]

---

[1] Dilute nitric acid may be used instead of sulphuric, *e. g*, when barium salts are present.

[2] A fairly concentrated potassium iodide solution is used to prevent the volatilization of iodine, and to aid in extracting the iodine from the carbon tetrachloride in the later titration with thiosulphate.

Titrate the liberated iodine with the standard sodium thiosulphate solution; shake the mixture continuously as the end-point is approached to ensure the rapid transfer of the iodine from the carbon tetrachloride to the potassium iodide solution.

In practice it is well to perform a preliminary titration to determine how much permanganate solution is required. The later analyses may then be quickly performed, since slightly less than this amount of potassium permanganate may be added before removing any iodine; but in this case, also, the mixture must be shaken vigorously at intervals.

If by accident an excess of permanganate be added while iodine is still present, and the formation of bromine or iodic acid be suspected, add a little sulphurous acid solution to again form the halide, and after 2 or 3 minutes treat with permanganate in the usual way.

The method was tested by means of a large number of analyses of potassium iodide solutions of known strength. The first group of analyses (Nos. 1–8) was made in connection with the investigation described in the following paper. The remaining analyses (Nos. 9–22) were made at a later date by one of us to supplement the first analyses and to determine the best conditions of analyzing iodide in the presence of chloride and bromide.

First Group of Test Analyses.

The carbon tetrachloride was not purified as directed in the procedure, and contained a trace of oxidizing material. In each of several blank analyses with approximately the same quantity of carbon tetrachloride as was used in an actual experiment, a slight amount of iodine was liberated which corresponded to about 0.06 cc. of the thiosulphate solution.

In the first analyses the sodium thiosulphate solution was 0.07348 normal. It was standardized: (1) by comparison with an iodine solution which had been titrated against arsenious oxide by the method described by Washburn[2] and (2) against a solution of copper sulphate by the method of Gooch and Heath,[3] the copper content of this solution having first been determined by electrolysis. The results of the two methods agreed within 0.1 per cent., but it is doubtful if this accuracy could be claimed for the copper standardization. The concentration of the permanganate solution was not determined.

---

[1] This second test of the end-point is valuable when bromide is present, for the permanganate color may then disappear, but the carbon tetrachloride becomes yellow, not pink.

[2] Washburn, THIS JOURNAL, 30, 31 (1908).

[3] Gooch and Heath, *Z. anorg. Chem.*, 55, 119 (1907); *Am. J. Sci.*, 24, 65.

The potassium iodide solution was prepared by dissolving in 1 liter 15.00 grams of the pure, dry salt (Kahlbaum's guaranteed reagent). This solution was analyzed by measuring out three 100 cc. portions and precipitating the iodide as silver iodide. The precipitate was washed thoroughly with warm water by decantation, collected upon a weighed platinum Gooch filter, heated at 200° for 12 hours, and weighed. The three determinations gave for the normality of the solution,[1] 0.09054, 0.09052 and 0.09057—mean 0.9054. These results are concordant, and the mean is probably more nearly accurate than the value, 0.09030, derived from a single observation of the weight of salt taken.[2]

The results of the first eight analyses are given in Table I. The first five are with potassium iodide alone; in the preliminary analysis (No. 4 in the table) excess of permanganate was added while iodine was still present, and was reduced by the sulphurous acid treatment described in the procedure. In the remaining three analyses 25 cc. 0.1 formal copper sulphate solution were also added, which resulted in the precipitation of cuprous iodide and thus subjected the method to a very severe test. The sulphuric acid concentration was varied greatly in these experiments. In each case the burette reading given in the last column of the table has been diminished by 0.06 in accordance with the blank experiments described above. The initial volume (second column) refers to the total volume of the aqueous solution at the beginning of the experiment. All numbers are cubic centimeters.

TABLE I.—TITRATION OF 25.05 CC. KI SOLUTION WITH 0.07348 NORMAL $Na_2S_2O_3$.

No.	Initial volume.	H_2SO_4 (1 20)	$CuSO_4$ soln. 0.1 normal.	$KMnO_4$ soln. added.	$Na_2S_2O_3$ soln (corrected).
1	75	2.5	..	15.4	30.80
2	75	25.0	..	15.4	30.82
3	75	25.0	..	15.4	30.85
4	75	25.0	..	15.6	30.86[3]
5	75	50.0	..	15.4	30.82
6	100	2.5	25	15.4	30.82
7	100	25.0	25	15.4	30.84
8	100	50.0	25	15.4	30.82

Mean, 30.82

---

[1] International atomic weights of 1908 were used in connection with the first group of analyses (Nos. 1–8). In the remainder of the work 1910 atomic weights were used. The weights of salts were not corrected to vacuum.

[2] This difference of 0.27 per cent. might be due to the presence of sodium iodide in the potassium iodide reagent.

[3] Preliminary experiment, rejected in taking the mean.

The concentration of the potassium iodide solution calculated from the mean burette reading (30.82 cc.) is 0.09041 normal, which is only 0.14 per cent. less than the value, 0.09054, given by the gravimetric analyses. An examination of the individual analyses shows that the extreme variation from the mean is 0.1 per cent., and that the result is not affected by a 20-fold variation in the concentration of sulphuric acid, nor by the presence of copper sulphate.

Other analyses made at the same time as the above gave equally satisfactory results. For example, the 0.1 and the 0.01 normal potassium iodide solutions, which were used in the conductance measurements described in an earlier paper,[1] were analyzed by this method. Four titrations of the first solution and two of the second were made. The normality obtained in the first case was almost identical with, and that in the second one about 0.1 per cent. greater than, the value calculated from the weight of the pure dry salt.

Second Group of Test Analyses.

The carbon tetrachloride used in the following analyses was purified as described in the procedure, with the result that no iodine was liberated in blank analyses and the uncertain correction applied in the above experiments was eliminated.

Two different thiosulphate solutions were used, and the relation between them was determined several times by comparing both with the same solution of copper sulphate.

The stock thiosulphate solution was standardized during the following experiments by Dr. W. D. Harkins against pure iodine[2] and was found to be 0.09577 normal. The corresponding concentration of the second thiosulphate solution was 0.1074. The latter solution was used in analyses 9–18 (Table II).

The second method of standardization tried was the comparison of one of the thiosulphate solutions with a $KMnO_4$ solution which had been standardized by Mr. A. C. Melcher against sodium oxalate. The $KMnO_4$ was added to excess of KI in a dilute sulphuric or acetic acid solution. The results were concordant, but the normality calculated for the thiosulphate solution was 0.3 per cent. less than that derived from the iodine standard. It is shown in an appendix to this paper that one-third to one-half of this difference is due to the conditions under which the permanganate solution had been standardized. There still remains, however, a discrepancy of 0.15 to 0.2 per cent. between the two standardizations, and it therefore seems improbable that the concentrations of the thiosulphate solutions derived from the iodine standard are too low.

---

[1] Bray and MacKay, This Journal, 32, 917 (1910).

[2] The iodine had been used in the experiments on the hydrolysis of iodine (Bray, This Journal, 32, 932 (1910)) and thus was free from soluble impurities, including chlorine and bromine. This was twice sublimed, and dried over calcium chloride for several days.

In the third method of standardization, however, in which the thiosulphate solutions were referred to copper as standard by the method used in the first analyses, the normalities were found from numerous careful experiments to be 0.0960 and 0.10765, *i. e.*, over 0.2 per cent. greater than those given by the iodine standard. The conclusion was finally reached that the absolute accuracy of the copper standard is not quite as high as we had at first supposed.[1]

---

[1] Since this result differs from that found in the standardization of the thiosulphate used in the first group of test analyses, it has seemed worth while to give the details of the final experiments.

The copper sulphate used was prepared from the commercial salt by recrystallizing once from sulphuric acid solution and twice from water. The copper content of the copper sulphate solutions was determined from several concordant electrolytic analyses, in which the copper was deposited from a dilute nitric acid solution on a rotating cathode. The apparatus was kindly placed at our disposal by Dr. E. B. Spear. The deposition of copper was shown to be practically complete by evaporating the solution nearly to dryness and adding ammonia.

The above normalities were derived from a series of titrations of each thiosulphate solution against the pure copper sulphate solution according to the directions of Gooch and Heath, using 5 g. potassium iodide in the presence of acetic acid and not allowing the volume to exceed 100 cc. Contrary to the statement of these investigators, the results were found to be less satisfactory in dilute sulphuric or hydrochloric acid than in acetic acid solutions. In the latter case the amount of iodine liberated after the completion of the titration was negligible in half an hour, while in the presence of sulphuric or hydrochloric acid at concentrations less than those recommended by Gooch and Heath the iodine liberated in this time corresponded to over 0.10 cc. of 0.1 normal thiosulphate, and the reaction continued at this rate for several hours. This reaction is undoubtedly the oxidation of hydriodic acid by oxygen; it was catalyzed by light, and possibly by the presence of the finely divided cuprous iodide precipitate. In the acetic acid solution the titration could be made slowly, and this was a great advantage in determining the end point.

As the end point was approached the color due to the presence of starch slowly faded, but the particles of cuprous iodide retained a slight but distinct dark color when the color in the solution was very faint. The most clearly defined end point was the change of color of the suspended precipitate from this dark shade to the yellowish white of pure cuprous iodide. The dark color of the cuprous iodide in the presence of iodine and starch indicates that iodine is adsorbed or dissolved by the cuprous iodide A possible explanation of the high thiosulphate concentration obtained in this standardization is that a trace of iodine is dissolved in the cuprous iodide and is not reduced by the thiosulphate.

In each titration from 30 to 40 cc. of thiosulphate were used, and the results were reproducible within 0.1 per cent. In the earlier experiments (in connection with the first group of analyses) a smaller volume was used, and the excess of thiosulphate added at the end point may have been a little greater than in the final experiments; both of these differences in treatment would lead to a relatively lower concentration for the thiosulphate in the first experiments.

Similar experiments were performed with a solution of commercial copper sulphate. (A small light-colored precipitate settled out in a few days and the clear solution was

The potassium iodide solution used in analyses Nos. 9–18 was prepared from the pure salt, which had been recrystallized from water. The crystals were heated for 16 hours at 150°, and 15.473 grams were dissolved and diluted to 1000.3 cc., at 25°, which corresponds to a normality of 0.09305. This value was thought to be a little high on account of the presence of a few particles of cork in the salt. Three 50 cc. portions (measured at 25°) were analyzed by Dr. W. D. Harkins by weighing silver iodide. To prevent occlusion of $AgNO_3$, the mixture was allowed to stand over night after the addition of slightly less than an equivalent amount of silver nitrate. The silver iodide precipitates were washed with cold water, and were heated 4 hours at 120° and 4 hours longer at 170°. The normalities found were 0.09285, 0.09292 and 0.09293; and the mean value, 0.09290, normal, was accepted as the concentration of the potassium iodide solution.

This solution was proved to be free from chloride by treating 100 cc. with permanganate according to the regular procedure to remove the iodide, heating the resulting solution with dilute nitric acid, filtering, and adding silver nitrate. Considerably less than 1 mg. of silver chloride was precipitated.

The results of the analyses of this solution are given in Table II. Chloride was present in Nos. 11 and 12, and bromide in Nos. 15–18. Blank experiments with potassium bromide alone under the conditions of analyses Nos. 15–18 showed that a drop of potassium permanganate was decolorized only very slowly in the dilute acid solutions (corresponding to those used in the experiments.) The thiosulphate concentrations were found to be slightly more than 0.1 per cent. greater than before. This difference disappeared or even changed sign when the $CuSO_4$ solution was treated with bromine, boiled long enough with dilute H_2SO_4 to expel the bromine, and then titrated in the usual way after adding excess of sodium acetate. It therefore seemed probable that the difference was due to the presence of a trace of ferrous sulphate or possibly of cuprous sulphate in the commercial copper sulphate.

TABLE II.—TITRATION OF 25.00 CC. KI SOLUTION WITH 0.1074 NORMAL $Na_2S_2O_3$.

No.	Initial volume.	H_2SO_4 (1.20).	KCl soln. 0.2 normal	KBr soln. 0.1 normal.	$KMnO_4$ soln. added.	$Na_2S_2O_3$ soln.
9	55	15	..	..	18.9	21.62
10	55	15	..	..	18.8+	21.62
11	55	15	10	..	18.85	21.63
12	55	15	10	..	18.85	21.62
13	55	2	..	..	18.84	21.62
14	110	5	..	..	18.82	21.62
15	110	2	..	10	18.82	21.62
16	115	3	..	10	18.8+	21.61
17	115	5	..	10	18.85	21.62
18	125	15	..	10	18.82	21.65

Mean, 21.62

ing to Nos. 15–16) but almost immediately in the most concentrated acid (corresponding to No. 18). The same observations were made in the actual experiments at the end point of the permanganate titration.

The results are seen to be remarkably concordant, and to be independent of the acid concentration, the volume of the solution and the presence of chloride. Bromide does not affect the result, provided that the concentration of the sulphuric acid is not too large. From these analyses, and the blank experiments already mentioned with bromide alone, the limiting concentration of acid is placed at about 5 cc. sulphuric acid (1.20) in 100 cc. aqueous solution.

From the mean burette reading (21.62), and the thiosulphate concentration based on the iodine standard, the potassium iodide solution is calculated to be 0.0929 normal, which is in perfect agreement with the concentration derived from the gravimetric analyses. The proof of the absolute accuracy of the titration is not quite complete, since slightly greater concentrations are calculated for this potassium iodide solution from the weight of potassium iodide taken, and by using the copper standard for the thiosulphate solution; but the results render it extremely probable that the use of pure dry potassium iodide as an iodometric standard would yield results accurate to within 0.1 per cent. This method of standardizing thiosulphate solutions has the following advantages: the results are perfectly reproducible; and the method is direct, since the iodine titrated was originally present in the potassium iodide weighed out. Since the iodine standard also has these advantages, and the copper standard does not, the rejection of the copper standard seems justifiable.

The question next examined was the relation between the amounts of potassium permanganate and sodium thiosulphate solutions used in these analyses. Under the existing conditions the oxidation of iodide by permanganate is essentially a direct titration of the iodide by the permanganate. The end point is definite, and the amount of potassium permanganate used in each experiment seldom differed by more than 0.1 per cent. from the mean value, 18.83 cc. It therefore seemed that it might be possible to use the permanganate titration in analyzing the potassium iodide solution, and thus dispense with the final thiosulphate titration. But when the permanganate solution was compared directly with thiosulphate by adding the permanganate to an excess of potassium iodide in a dilute acid solution and titrating the liberated iodine, it was found that 18.83 cc. of the permanganate solution was equivalent to 21.73 cc. thiosulphate solution, instead of 21.62 cc. as expected. The difference 0.11 cc. is the error in the permanganate titration of iodide; and, since the error may depend upon the experimental conditions, it is evident that the permanganate titration could be used only as an empirical method, and might not be reliable, if the conditions were altered.

The reason for this error was found to be the incomplete reduction of permanganate to the manganous state when the iodide was not present in excess. The amount of oxidizing material present in the aqueous solution, after the permanganate titration had been completed and the iodine removed, was determined in No. 14 by adding a little potassium iodide to the aqueous solution in the separating funnel; the iodine liberated was equivalent to 0.09 cc. thiosulphate, while, judging from the color, the amount of permanganate present corresponded to only 0.01 cc. The number 0.09 is the error in the permanganate titration, and it is thus possible by this method to measure this error directly.

In the final experiments (Nos. 19–22) this direct method was used to determine the error in the permanganate titration. The amounts of thiosulphate solution used are given in the last column of Table III under the heading "$KMnO_4$ error;" the values in Nos. 19 and 20 are only approximate; the more accurate ones in Nos. 21 and 22 were derived from results obtained by using a dilute thiosulphate solution. The amount of thiosulphate solution equivalent to the mean amount (19.97 cc.) of permanganate solution was determined in the presence of excess of iodide to be 25.82 cc. On subtracting the experimentally determined value of the "$KMnO_4$ error," 0.10, the result, 25.72, is seen to agree almost exactly with the thiosulphate titration, 25.71 cc.

The results of all the experiments (Nos. 9–22) show that there is a 0.4–0.5 per cent. error in the direct titration of iodide by permanganate due to the incomplete reduction of permanganate to the manganous state. The possibility that this error is present in other permanganate titrations is considered in a note at the end of this article.

In the final experiments the stock 0.09577 normal, thiosulphate solution was used.

The potassium iodide solution was prepared from Merck's "neutral reagent," which contained chloride, by dissolving 16.614 grams of the dry salt and diluting to one liter. Three 50 cc. portions were analyzed by Dr. Harkins; the average weight of the silver iodide plus silver chloride precipitate was 1.793 grams. Two 50 cc. portions were analyzed for chloride, after removing the iodide by the regular procedure with permanganate; the mean weight of silver chloride was. 0.0242 gram. The difference between 1.793 and 0.0242 gave the weight of silver iodide, from which the potassium iodide concentration was calculated to be 0.09840 normal. A similar correction of the weight of salt taken for the weight of potassium chloride present (corresponding to the amount of silver chloride found) led to the normality 0.09856. The result based on the weight of the silver salts is considered the more accurate; the difference of 0.16 is probably due to the presence of a trace of impurity other than chloride in the potassium iodide reagent.

The results are presented in the following table. The meaning of the results in the last column has already been explained.

TABLE III.—TITRATION OF 25 00 CC. OF A KI SOLUTION WITH 0.09577 NORMAL $Na_2S_2O_3$.

				$Na_2S_2O_3$ solution	
No.	Initial volume cc	H_2SO_4 (1 20). cc.	$KMnO_4$ solution cc.	$Na_2S_2O_3$ titration.	$KMnO_4$ error.
19	100	5	20 4	25 72	0.07
20	100	5	19.97	25 71	0.08
21	100	5	19 97	25 71	0 10
22	100	5	19 98	25 71	0 10

In experiment 19 a considerable excess of $KMnO_4$ was added while a large amount of iodine was still present, and the supplementary treatment with sulphurous acid was used. The fact that no error is introduced by this treatment is established by the accuracy of the final thiosulphate titration, 25.72 cc.

From the mean value of the thiosulphate titration the concentration of potassium iodide is calculated to be 0.09849, which is intermediate between the two values derived above from the weights of the silver and of the potassium salts, and does not differ from either by more than 0.1 per cent.

Summary.

In this article a method of determining iodide in aqueous solution has been described, which depends upon the oxidation of the iodide to iodine by permanganate, the removal of the liberated iodine by carbon tetrachloride, and the titration of this iodine with a standard sodium thiosulphate solution.

The test analyses (Tables I–III) with potassium iodide solutions of known concentrations show that the titration results are perfectly reproducible, and independent of the presence of chloride, bromide or copper sulphate.

From the standpoint of absolute accuracy this method is also satisfactory, since the results agreed within less than 0.1 per cent. with those based on iodine as standard. Pure, dry potassium iodide may therefore be recommended as an iodometric standard.

Two other iodometric standards yielded less satisfactory results. From a single series of experiments with a permanganate solution, standardized against sodium oxalate, the concentration of a stock sodium thiosulphate solution seemed to be about 0.15 per cent. too low; while from careful experiments with a copper sulphate solution, standardized by weighing electrolytically deposited copper, the concentration of the thiosulphate solution was found to be about 0.2 per cent. too high.

In the method of analysis here described the treatment with permanganate is essentially a direct titration of iodide by the permanganate. It is impossible, however, to replace the thiosulphate titration by this permanganate titration, since the reduction of permanganate to the manganous state was found to be not quite complete, and the resulting error corresponded to about 0.10 cc. (or 0.4–0.5 per cent.) of the permanganate solution. This error was measured directly by adding a little potassium iodide to the aqueous solution (after the removal of the carbon tetrachloride) and titrating the iodine then liberated.

BOSTON, July, 1910.

A SOURCE OF ERROR IN PERMANGANATE TITRATIONS; PRELIMINARY NOTE.

BY W. C. BRAY.

Received July 25, 1910.

In the direct titration of iodide by permanganate described in the preceding article, the permanganate was found to be incompletely reduced to the manganous state, and the resulting error was about 0.10 cc. of the 0.12 normal permanganate solution. It is therefore evident that in this reaction,

$$MnO_4^- + 5I^- + 8H^+ = Mn^{++} + 2^1/_2 I_2 + 4H_2O,$$

the reduction of the permanganate takes place in stages, and that the final stage takes place more slowly than the reaction involving the disappearance of permanganate.[1]

Since the reduction of permanganate undoubtedly takes place in stages in other reactions, a similar error is possible in other permanganate titrations, and indeed is to be expected wherever the final stage of the reaction is known to take place relatively slowly. Apparently such a case is furnished by the titration with oxalic acid; for the kinetic experiments of Skrabal[2] have shown that the reduction from the manganic to the manganous state by oxalic acid is a slow reaction, and that a stable complex is formed between the manganic salt and oxalic acid.

Accordingly the following experiments (Table IV) were undertaken to determine under what conditions the error due to incomplete reduction of permanganate was appreciable in the oxalic acid titration. As in the previous experiments (Table III), this error was measured directly, by adding a little potassium iodide to the cold solution after the permanganate end point had been reached, and titrating the liberated iodine with thiosulphate. A dilute thiosulphate solution was used and the corresponding volume of the permanganate solution is recorded in the last column of the table.[1] This result includes the "blank" correction due to the excess of permanganate added to produce the end point, which from the color was estimated not to exceed 0.01 cc. in Nos. 1 and 2, in which the volume was small, and 0.02 cc. in the remaining experiments.

---

[1] That the incomplete reduction of the permanganate is due to an equilibrium involving iodine, such as $Mn^{+++} + I^- = Mn^{++} + ^1/_2 I_2$, seems improbable, since the concentration of the iodine is kept at a very small value by the presence of the carbon tetrachloride phase.

[2] Skrabal, *Z. anorg. Chem.*, 42, 1 (1904).

In each experiment (except No. 8) a 25 cc. portion of pure sodium oxalate solution was mixed with a known amount of sulphuric acid; the mixture after dilution to the volume given in the table was heated to 90°, and the permanganate solution was added from a burette. In the last four experiments, after about 80 per cent. of the oxalate had been oxidized, the mixtures were cooled, and the titration completed at about 25°. In all cases the end point was approached very carefully, and the last drops were added slowly. In experiments 1-4 the end point was sharply defined; in Nos. 5-8 the pink color seemed to fade very slowly, but no extra permanganate was added. In Nos. 9 and 10, however, when the acid concentration was very large, the first pink color faded quickly and more permanganate was added; and at the low temperatures the end point was even less definite, especially at the large acid concentrations (Nos. 13 and 14). In experiments 2, 3, 4, and 11 the solution became slightly brown during addition of permanganate, but on standing this color disappeared, rapidly at the high temperature and slowly at the low.

TABLE IV.—TITRATION OF SODIUM OXALATE WITH 0.1 NORMAL $KMnO_4$.

Expt. No.	Oxalate solution cc.	H_2SO_4 (1 : 20) cc.	Initial volume. cc.	Final temp. about	$KMnO_4$ solution, 0.12 N	
					Titration cc.	Error cc.
1	25	10	50	80°	21.20	0.02
2	25	10	300	80	21.23	0.03
3-4	25	10	300	80	.	0.03
5	25	50	300	80	21.26	0.05
6-7	25	50	300	80	.	0.05
8	75	50	300	70	.	0.06
9	25	250	300	80	21.26	0.07
10	25	250	300	80	.	0.06
11	25	10	50	25	21.29	0.07
12	25	10	300	25	21.27	0.06
13	25	50	300	25	21.32	0.11
14	25	250	300	25	21.35	0.14

From an examination of the table it is seen that when the amounts of permanganate solution used are diminished by the numbers in the last column, the values are nearly constant, with a mean value 21.20. It is obvious that this is the amount of permanganate actually equivalent to 25 cc. of the oxalate solution, and that the numbers in the last column show the errors under different experimental conditions.

---

[1] It was shown that the liberation of iodine in the concentrated acid solutions was not due to the action of oxygen on hydriodic acid by allowing the mixtures to stand for half an hour after the titration and determining the amount of iodine liberated in that time.

On deducting the blank experiment correction, the error in the first four experiments, due to the incomplete reduction of the permanganate, is seen to be only 0.01 cc., which is negligible when the amount of permanganate used is sufficiently large. The most favorable conditions for the titration, therefore, are a small amount of acid and a final temperature of 70 or 80°. Since these conditions are those recommended in books on quantitative analysis[1] it is evident that the error due to the incomplete oxidation of permanganate need not ordinarily be taken into account.

The large errors in the remaining experiments show the importance of avoiding the following unfavorable conditions in titrating: low temperature, high acid concentration and large volume. In the last experiment, for example, the error was 0.14 cc. of which only 0.02 was due to permanganate alone.

A comparison of experiments 6 and 8 shows that the absolute error remained nearly constant (and the percentage error decreased greatly) when the concentration of manganous salt was increased threefold. This result was confirmed by a pair of experiments, in one of which a large excess of manganous sulphate was added initially. In the standardization of permanganate referred to in the preceding paper the titrations were made under the same conditions as in experiments 6–8, the volume of permanganate varied between 40 and 60 cc., and no blank correction was applied for the excess of permanganate. It follows therefore, as already pointed out, that the error in this standardization was 0.10–0.15 per cent.

From the present results it is evident that an error due to incomplete reduction of permanganate is possible in titrating other reducing agents, and that each case must therefore be carefully investigated if an accuracy of 0.1 per cent. is desired. In many instances, however, the above direct method cannot be used in determining the error. For example, in the ferrous sulphate titration the ferric sulphate formed would itself cause the liberation of iodine. In such cases the constancy of the results under widely different conditions of temperature and acid concentration would probably insure the accuracy of the method of titration. This conclusion would also be confirmed if in an investigation of the reduction of a manganic salt by the reducing agent, as ferrous sulphate, it were found that the reaction takes place rapidly and completely.

These experiments will not be continued by the author at the present time, but the question whether there is an appreciable error in the ferrous sulphate titration will doubtless be settled in the near future by the investigation of the oxalate and ferrous sulphate titrations now in progress at the Bureau of Standards. The author takes pleasure in thanking Dr. W. F. Hillebrand and Mr. R. S. McBride, of the Bureau of Standards, for their kindness in reading and criticizing this note before its publication.

---

[1] Treadwell, "Hall's Translation, II, 479, recommends a temperature of 70°, 10 cc. H_2SO_4, and a volume of 200 cc

BOSTON, July, 1910

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 55.]

THE EQUILIBRIUM BETWEEN SOLID CUPROUS IODIDE AND AQUEOUS SOLUTIONS CONTAINING CUPRIC SALT AND IODINE.

BY W. C. BRAY AND G. M. J. MACKAY.

Received July 25, 1910

This investigation was originally undertaken in order to test the generally accepted view that the cuprous ion is monatomic (Cu^+), rather than diatomic (Cu_2^{++}), and especially to check the results of Bodländer and Storbeck[1] on this subject. The work, however, was interrupted two years ago and has not been continued; the results then obtained are presented in the present article as an investigation of the law of mass action in dilute aqueous solutions.

Cuprous iodide is difficultly soluble in water, but in the presence of iodine a considerable amount dissolves, owing to the formation of cupric iodide and tri-iodide. The following two equilibria are involved:

$$CuI \text{ (solid)} + \tfrac{1}{2}I_2 = Cu^{++} + 2I^-, \text{ and } I_3^- = I_2 + I^-.$$

From the experimental results at 25° presented below, values have been determined, under widely different conditions, for the two equilibrium functions:

$$(Cu^{++})(I^-)^2/(I_2)^{\frac{1}{2}} = K', \text{ and } (I^-)(I_2)/(I_3^-) = K.$$

Bodländer and Storbeck have reported a single, apparently not very accurate experiment at room temperature (18–20°), in which 1 liter of solution saturated with both cuprous iodide and iodine was found to contain 0.01666 gram molecule of cupric salt, and 0.00946 equivalent of dissolved iodine.

The *cuprous iodide* was prepared according to the directions of Bevan Lean,[2] by adding one formula weight of potassium iodide dissolved in 150 cc. of water to a solution of one formula weight of copper sulphate dissolved in 1500 cc. of water saturated with sulphur dioxide. The resulting precipitate was washed several times with water containing sulphur dioxide, and finally with pure water until all trace of sulphate had disappeared. In each of our equilibrium experiments a large excess (about 20 grams) of solid cuprous iodide was present.

---

[1] Borländer and Storbeck, *Z. anorg. Chem.*, **31**, 469 (1902).

[2] *J. Chem. Soc.*, **73**, 149 (1898).

The experimental methods of obtaining saturated solutions, removing known volumes for titration, making conductance measurements, etc., were the same as were used in determining the solubility of iodine in potassium iodide solutions.[1]

The concentration of *iodine*, whenever the solid was present, was assumed to be 0.00132 molecule I_2 per liter, as determined in a recent investigation.[2] In the three remaining experiments (Nos. 1–3), in which solid iodine was absent, the equilibrium was investigated in the presence of carbon tetrachloride. The concentration of iodine in this phase was determined by titration; that in the aqueous phase was calculated by means of the partition-coefficient of iodine between carbon tetrachloride and water. The determinations of the latter were made in the presence of iodine; after 24 hours' rotation the ratio of the concentration in carbon tetrachloride to that in water was found to be 90.8 and 89.3. The smaller value agrees fairly well with that determined by Yakovkin,[3] 89.55, in the presence of solid iodine. After taking into consideration the fact that, on account of the hydrolysis of iodine in the aqueous solution, these values should be increased by about 0.08 per cent., the value 90 was chosen Yakovkin's results, however, show a decrease of the partition coefficient with decreasing iodine concentration, and, even after correcting for hydrolysis, it is possible that a value as low as 86.5 should be used in our experiments. The calculations for exps. Nos. 1–3 were accordingly repeated, using this partition coefficient and the results are given in Table II as experiments Nos. 1*a*, 2*a*, and 3*a*.

In addition to molecular iodine, the solutions contained three constituents to be determined: copper, ΣCu; iodide, ΣI; and tri-iodide, $\Sigma I_3'$; and three separate analyses were made in each case.

The *copper* was determined, usually in 100 cc. of solution, by evaporating the solution with 5–10 cc. of dilute sulphuric acid and a few drops of nitric acid until white acid fumes were given off. Ammonia was then added in slight excess, and the solution boiled to expel the excess of ammonia. Finally 50 cc. of 25 per cent. acetic acid and 5 grams of potassium iodide were added, and the mixture was titrated with sodium thiosulphate solution according to the method investigated by Gooch and Heath.[4] Another portion of the saturated solution was titrated in a similar manner directly with thiosulphate, which gave the *total dissolved iodine* and copper. Finally, in a third portion, the *total iodine* was determined by the method described in the preceding paper. Thus the three analyses were referred to a single thiosulphate solution, and the error in determining differences reduced to a minimum. The thiosulphate was standardized by comparison with a known arsenious acid solution, and checked against a known copper sulphate solution, as explained in the first group of analyses in the preceding article.

---

[1] Bray and MacKay, THIS JOURNAL, 32, 918 (1910).

[2] Bray, THIS JOURNAL, 32, 936 (1910).

[3] Yakovkin, *Z. physik. Chem.*, 18, 585 (1895).

[4] Gooch and Heath, *Am. J. Sci.*, 24, 65 (1907); *Z. anorg. Chem.*, 55, 119 (1907).

The method of calculating the concentrations of the separate substances is illustrated by the following example (Expt. No. 4):

$$\begin{array}{lll} \text{Total iodine} & \Sigma I + 3\Sigma I_3 + 2I_2 & = 0.08490 \\ \text{Direct titration} & \Sigma Cu + 2\Sigma I_3 + 2I_2 & = 0.06432 \\ & \Sigma Cu & = 0.02068 \\ & 2I_2 & = 0.00264 \end{array}$$

From these four equations ΣI_3 and ΣI are calculated to be 0.02050 and 0.02076, respectively.

In the solutions to which no copper salt or iodide had been added a check is furnished upon the accuracy of our analyses by the stoichiometric relation that the equivalent concentration of copper should equal the sum of the concentrations of iodide and triiodide,[1] $2\Sigma Cu = \Sigma I + \Sigma I_3$. In the above example these numbers are 0.04136 and 0.04126, respectively; this difference corresponds to an error of only 0.12 per cent. in the determination of the total iodine, or to larger and less probable errors in the determination of copper or in the direct thiosulphate titration. Accordingly, we have adopted the value of 0.02086 instead of 0.02076 for the value of ΣI, and have applied similar corrections to ΣI in the other experiments in which this stoichiometric relation could be used, except in that with nitric acid (No. 11) where the deviation is much larger and may be accounted for by a reaction between hydriodic acid and oxygen.

The experimental results are presented in Table I. The values given in the column "ΣI calculated" are derived from the relation $2\Sigma Cu = \Sigma I_3 + \Sigma I$, and have been adopted in the calculations described below. The values of "specific conductance, calculated" are derived from the concentrations of the separate ions given in Table II, by means of the following equivalent conductances at 25°, $\Lambda_{Cu} = 56.0$, $\Lambda_{I} = 76.5$, $\Lambda_{I_3} = 41.5$, $\Lambda_{K} = 74.8$, $\Lambda_{NO_3} = 70.6$.

---

[1] We have neglected the cuprous copper in solution; this is present as cuprous iodide and as a complex ion, CuI_2^-, formed by the union of cuprous iodide and iodide ion. With regard to the first substance, Bodländer and Storbeck (*loc. cit.*, page 427) have calculated from electromotive force measurements, that the solubility product $(Cu^+)(I^-)$ is equal to 5×10^{-12}; since in our experiments the concentration of I^- never is less than 0.0088, it is evident that the concentration of Cu^+ cannot exceed 0.6×10^{-9}. The same authors have shown (page 475) that the ratio $(CuI_2^-)/(I^-)$ in the presence of solid CuI is not greater than 7.8×10^{-4}. This complex is therefore present in greatest amount in expt. No. 7, where I^- has its maximum concentration, and the amount does not exceed 2×10^{-5} g. molecule CuI_2^- per liter; this corresponds to only 0.2 per cent. of the total copper present, and its neglect does not seriously alter the final results.

The time of rotation of two days was adopted after preliminary experiments with water alone, in which it was found that the concentration of copper salt after 24 hours was a few tenths of a per cent. less than that obtained after 48 hours. In No. 5 the equilibrium was approached from undersaturation, and in No. 4 from supersaturation, attained by first rotating the mixture for several hours at 35°. The agreement shows that the equilibrium is actually reached in 2 days. This conclusion is further justified by the similar results obtained in experiments Nos. 9 and 10, where the times of rotation differed by 2 days.

TABLE I.—EXPERIMENTAL RESULTS.

				Concentrations, millimols per liter.					Specific cond. × 10^6.	
No.	Solid phases.	Solvent.	Days rotated.	I_2.	Σ Cu.	Σ I_3	ΣI expt.	ΣI calc.	Measured.	Calculated.
1	CuI	Water and CCl_4 (part. coeff. = 90).......	2	0.1007	8.18	1.125	15.18	15.24	1853	1824
2	"	(Part. coeff. = 90)...	2	0.1501	9.01	1.76	16.20	16.26	1979	1980
3	"	(Part. coeff. = 90)....	2	0.8040	15.78	11.58	19.83	19.98	3139	3[illegible]98
4	CuI, I_2	Water alone.........	2	1.32	20.68	20.50	20.76	20 86	3848	3834
5	"	Water alone.........	2	1.32	20.71	20.53	20.76	20 89	3877	3840
6	"	Acetic acid (0.1*N*)...	2	1.32	27.16	21.29	20.78	21.03	....	....
7	"	KI solution.........	2	1 32	10.03	31.75	31.77	.....	6923	6913
8	"	$CuSO_4$ solution......	2	1.32	101.7	15.67	16.01	.....	....	....
9	"	$Cu(NO_3)_2$ solution....	2	1 32	100.0	12.41	13 14	.....	1721	1749
10	"	$Cu(NO_3)_2$ solution....	4	1.32	111.3	11.89	12 78	.....	1892	1926
11	"	HNO_3 (0.113*N*).....	2	1.32	24.11	23.90	23.31	.....	....	....
12	"	$Mg(NO_3)_2$ (0.1*F*)....	2	1.32	25.77	24.77	26.69	26.77	....	....
13	"	$Mg(NO_3)_2$ (0.1*F*).. HNO_3 (0.005*N*)...	2	1.32	25.77	24.58	26.73	26.96	....	....

The concentrations of the separate ions and of the various un-ionized substances were calculated by the method of approximations which has already been explained in publications from this laboratory.[1] This depends upon the assumption that the "ionization function" of a given salt, K = (anion)(cation)/(un-ionized salt), for example $(Cu^{++})(I^{-})/(CuI_2)$ for cupric iodide, depends only on the equivalent ion concentration, and has the same value in a mixture as at the same ion concentration in a solution of the pure salt.

In the present instance accurate conductance data at 25° are not available, and the calculations are based on the following assumptions: The ionization values for CuI_2, $Cu(I_3)_2$, $Cu(NO_3)_2$, $Cu(Ac)_2$, and $Mg(NO_3)_2$ are equal to the values for $MgCl_2$ calculated from the data of Kohlrausch and

---

[1] Cf. THIS JOURNAL, 31, 754 (1909).

Grüneisen[1] at 18° taking $\Lambda_0 = 111.4$; those for KI, HI, HI_3, and HNO_3 are the values of KCl at 18° ($\Lambda_0 = 130.1$),[2] which are practically equal to our own values of KI at 25°;[3] and those for $CuSO_4$ are the values of this salt at 18° ($\Lambda_0 = 115.7$).[1] The ionization constant of acetic acid was assumed to be 1.8×10^{-5} at 25°.

The validity of these assumptions may be tested in the case of CuI_2 and $Cu(I_3)_2$ by a comparison of the calculated and measured conductances (Table I) in experiments Nos. 1-5 and 7. Since ordinary distilled water was used in these experiments the measured specific conductances must be reduced by from 2 to 5×10^{-6}, and it is at once evident that the agreement is then a satisfactory one. In experiments Nos. 9 and 10 the agreement is less satisfactory, which indicates that the degree of ionization of $Cu(NO_3)_2$ is less than that of CuI_2; a correction of 2 per cent., however, alters the value of the equilibrium function K' only from 1.62 to 1.59×10^{-4}, since the concentration of I^- remains practically unchanged.

The results of the calculations are presented in Table II Concentrations are expressed in millimols per liter in the table, but all calculations are based on molal concentrations.

TABLE II CALCULATION OF EQUILIBRIUM FUNCTIONS.

		Concentrations millimols per liter						
Expt. No.	Solvent	I_2	Cu^+	I^-	I_3^-	Equiv Ion	$K \frac{(I^-)(I_2)}{(I_3^-)}$	$K' \frac{(Cu^+)(I^-)^2}{(I_2)^{\frac{1}{2}}}$
1	Water and CCl_4 (Part. coeff. = 90)	0.1007	7.01	13.06	0.065	14.02	1.37×10^3	1.19×10^4
2	(Part. coeff. = 90)	0.1501	7.67	13.84	1.50	15.34	1.39×10^3	1.20×10^4
3	(Part. coeff. = 90)	0.8040	12.94	16.38	9.50	25.88	1.39×10^3	1.23×10^4
1*a*	Water and CCl_4 (Part. coeff. = 86.5)	0.1047	7.01	13.06	0.96	14.02	1.42×10^3	1.17×10
2*a*	(Part. coeff. = 86.5)	0.1562	7.67	13.85	1.49	15.34	1.45×10^3	1.18×10^4
3*a*	(Part. coeff. = 86.5)	0.8364	12.94	16.41	9.47	25.88	1.45×10^3	1.21×10^4
4	Water	1.32	16.65	16.80	16.50	33.30	1.34×10^3	1.29×10^4
5	Water..	1.32	16.67	16.82	16.52	33.34	1.34×10^3	1.30×10^4
6	Acetic acid (0.1*N*)	1.32	16.97	16.94	17.14	35.35	1.30×10^3	1.34×10^4
7	KI solution.. .	1.32	7.76	26.94	26.92	53.86	1.32×10^3	1.55×10^4
8	$CuSO_4$ solution . .	1.32	38.45	11.93	11.68	76.91	1.35×10^3	1.51×10^4
9	$Cu(NO_3)_2$ solution..	1.32	69.85	9.18	8.66	139.70	1.40×10^3	1.62×10^4
10	$Cu(NO_3)_2$ solution	1.32	76.80	8.82	8.20	153.60	1.42×10^3	1.64×10^4
11	HNO_3 (0.113*N*).	1.32	16.81	18.63	19.10	128.13	1.29×10^3	1.61×10^4
12	$Mg(NO_3)_2$ (0.1*F*) .	1.32	17.53	18.20	16.86	171.06	1.42×10^3	1.60×10^4
13	$Mg(NO_3)_2$ (0.1*F*). + HNO_3 (0.005*N*)	1.32	17.48	18.36	16.74	174.80	1.45×10^3	1.62×10^4

---

[1] Kohlrausch and Grüneisen, *Landolt-Bornstein-Meyerhoffer*, page 745.

[2] Kohlrausch and Maltby, *Ibid.*, page 744.

[3] THIS JOURNAL, 32, 920 (1910).

An examination of the values of the equilibrium function $K = (I^-)(I_2)/(I_3^-)$ shows that in the first three experiments the values based on the partition coefficient 90 are lower and in better agreement with the remaining values than those based on the partition coefficient 86.5. Accordingly the results tabulated at Nos. 1–3 are accepted rather than Nos. 1*a*–3*a*. In neutral solutions the values of K lie between 1.32 and 1.42×10^{-3} while in acid solution (Nos. 6 and 11) the values are slightly lower.[1]

In agreement with the results in potassium iodide solutions,[2] the deviations from the law of mass action are in the direction that the values of K decrease with increasing iodide concentration. Thus when the total concentration of salt (iodide and tri-iodide) increases from 0.018 (Exp. 2) to 0.063 (Exp. 7) the values of K are 1.39 and 1.32×10^{-3}, respectively—in good agreement with the corresponding values in the potassium iodide solutions, 1.38 and 1.33×10^{-3}. From the present experiments it is evident that the presence of other salts, as copper nitrate in Nos. 8 and 9 or magnesium nitrate in No. 12, does not cause a similar decrease in the value of K. In the earlier investigation with potassium iodide solutions the conclusion was reached that the decrease of K with increasing concentration of the salt was due mainly to a decrease in the ratio of the activity[3] of tri-iodide ion to its concentration. The present experiments enable the additional conclusion to be drawn that in this reaction this influence of the salt is not general for all salts but is an individual effect for iodide-tri-iodide solutions.

From the values of the second equilibrium function $K' = (Cu^{++})(I^-)^2/(I_2)^{\frac{1}{2}}$, it is evident that this reaction conforms to the law of mass action as far as the influence of iodine is concerned. Thus K' is increased only 9 per cent. as a result of a 13-fold increase in the concentration of iodine (Expts. 1 and 4). Furthermore K' is almost unaltered by the presence of acetic acid (Nos. 5 and 6).

In the remaining experiments, however, the deviations from the law of mass action are very marked. Thus K' shows a 19 per cent. increase when the concentration of iodide ion is increased 60 per cent. (Nos. 5 and 7), and a 26 per cent. increase when the concentration of cupric ion is increased 4.6-fold (Nos. 5 and 10). Finally there is the striking effect of the presence of a salt without a common ion, as magnesium nitrate or nitric acid, which results in a 23 to 25 per cent. increase in K' (No. 5 and Nos. 11–13).

A closer examination of these results leads to the conclusion that in this reaction there is a relationship between the deviation from the mass law and the total ion or salt concentration. Thus the values of K' show a steady increase with increasing equivalent ion concentration, which is roughly independent of the nature of the salts present. To enable this relation to be easily seen, the experiments have been arranged in the table in the order of increasing ion concentration.

---

[1] Cf. Dawson, *J. Chem. Soc.*, **79**, 238 (1907).

[2] Bray and MacKay, THIS JOURNAL, **32**, 924 (1910).

[3] Cf. Lewis, *Proc. Am. Acad.*, **43**, 259 (1907); *Z. physik. Chem.*, **61**, 129 (1907).

This result is in perfect agreement with the results of other investigations in aqueous solutions, such as the determination of the electromotive force of concentration cells, or the effects of salts on the solubility of another salt. Thus, as pointed out in an earlier paper,[1] existing evidence indicates that in the case of a single ion the activity (A) increases somewhat less rapidly than its concentration (C) (when the latter is derived from conductance measurements), or in other words, that the ratio A/C decreases with increasing ion concentration. By taking into consideration the law (based on the definition of activity) that the activity function $A_{Cu^{++}} \times A^2_{I^-}/A^{\frac{1}{2}}_{I_2}$ is constant under all conditions, it could have been predicted as probable that the equilibrium (concentration) function $K' = C_{Cu^{++}} \times C^2_{I^-}/C^{\frac{1}{2}}_{I_2}$ would increase with increasing ion concentration, which is the experimental result derived from the present measurements.

Finally, it is interesting to note that, when solid CuI and I_2 are both present, the equilibrium function $(Cu^{++})(I^-)^2$ has the same form as the solubility product of a hypothetical, difficultly soluble cupric iodide. It is therefore to be expected that the results of the present investigation will be similar to those derived from investigations of the solubility of a salt in the presence of other salts. Accordingly the increase in the value of K' in Expts. 5 13 indicates that under similar conditions the solubility product of a difficultly soluble salt will not be constant, but will increase with increasing ion concentration. This conclusion is in agreement with the results of solubility investigations already obtained in this laboratory, which will soon be published.

Summary.

The equilibrium

$$CuI(solid) + \tfrac{1}{2}I_2 = Cu^{++} + 2I^-$$

has been investigated at 25° under widely different conditions. The ionic concentrations in the various mixtures were calculated by means of the empirical relations derived from conductance measurements.

The values of the equilibrium function $K' = (Cu^{++})(I^-)^2/(I_2)^{\frac{1}{2}}$ show that this equilibrium conforms with the law of mass action only as far as the influence of iodine is concerned, and deviates from it when cupric salt, iodide, or other salt is added. In all these cases, however, the deviations are of such a nature that K' increases with increasing ion concentration.

---

[1] Bray and MacKay, *Loc. cit.* In the e. m. f. measurements of concentration cells by Jahn and by Lewis and von Ende, formerly cited as examples of this rule, the ratio A/C was practically constant at low concentrations, but the decrease was marked in 0.1 normal solutions.

This result, when examined from the standpoint of activity, as defined by Lewis, furnishes another illustration of the apparently general rule that when the concentration of an ion is based on conductance measurements the ratio of its activity to its concentration decreases somewhat with increasing ion concentration. An important consequence of this rule is that the solubility product of a salt will not be exactly constant but will increase with increasing ion concentration.

Values were also calculated for anothor equilibrium function $K = (I^-)(I_2)/(I_3^-)$. The results confirm the conclusion reached in an earlier paper that K decreases with increasing concentration of iodide, but show that other salts do not produce a similar effect.

Conductance measurements were also made with a number of the equilibrium solutions. These show that cupric iodide and cupric tri-iodide are ionized to the same extent as magnesium chloride, and that cupric nitrate is ionized to a somewhat less extent.

BOSTON, July, 1910.

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY OF NEW YORK UNIVERSITY.]

THE POTENTIAL OF IRON CALCULATED FROM EQUILIBRIA MEASUREMENTS.[1]

BY ARTHUR B. LAMB.

Knowing the dissociation pressure of a metallic oxide, its heat of formation, the change of its heat of formation with the temperature, the solubility of its oxide in water, and finally, knowing the single potential of the oxygen electrode, it is possible to calculate on the basis of the fundamental laws of energetics and the concentration law the potential of the metal against a normal solution of its ions.[2]

Many metals give fairly definite and easily measurable potentials, especially when an amalgamated electrode can be employed.[3] When this is the case, an indirect calculation, such as the one just outlined, depending upon measurements of such difficulty as the dissociation pressures of metallic oxides at high temperatures, would be disadvantageous. The reverse calculation, that is, the calculation of dissociation pressures from electromotive forces, would be more rational, and indeed, has most often been made. This is not, however, always the case. Many solid metals give rather variable potentials, and certain metals, such as iron, have yielded widely differing values of the potential. Thus Richards and Behr[1] found that the true potential of iron was apparently as high as 0.18 volt, for the porous form, and 0.15 volt for the massive, if the calomel electrode is taken as —0.56, while other investigators had obtained values about a tenth of a volt lower. It is evident that in such a case as this a calculation of the potential from equilibria measurements might well be of interest.

---

[1] Presented in preliminary form before the New York Section, Dec. 11, 1908.

[2] van't Hoff, Ostwald's Klassiker No. 110, pp. 76 and 103 (1885); also Lewis, THIS JOURNAL, 28, 162 (1906). *Z. physik. Chem.*, 55, 470 (1906).

[3] Lewis, THIS JOURNAL, 32, 732 (1910).

Unfortunately, measurements of the equilibrium between iron, ferrous oxide and oxygen have not been made. It is certain, too, that such measurements would be very difficult of execution, for the temperature necessary to produce a measurable dissociation of the ferrous oxide would be very high. However, equilibrium measurements upon the system iron, ferrous oxide, carbon monoxide and carbon dioxide can be used for the desired calculation, just as well as the direct measurement of the dissociation pressure of the ferrous oxide; for our knowledge of the carbon monoxide, carbon dioxide and oxygen equilibrium is relatively very satisfactory. By combining the equations for these two equilibria we can easily calculate the dissociation equilibrium of ferrous oxide.

Baur and Glaessner[2] have made the necessary measurements of the equilibrium between iron, ferrous oxide and mixtures of carbon monoxide and dioxide. They found that at 1000° absolute, a mixture containing 40 per cent. carbon dioxide and 59 per cent. carbon monoxide was in equilibrium with a mixture of iron and ferrous oxide at atmospheric pressure. We can now calculate from the results of Nernst and v. Wartenberg[3] what the partial pressure of the oxygen must have been in this mixture of carbon monoxide and dioxide at this temperature. They found that at 1000° absolute and at atmospheric pressure carbon dioxide is 1.58×10^{-5} per cent. dissociated. Since

$$K_p = \frac{p_{CO_2}}{P_{CO} \times p_{O_2}^{1/2}}$$

where K_p represents the equilibrium constant expressed in units of pressure, and p_{CO_2}, p_{CO}, p_{O_2} the respective partial pressures, it follows that

$$K_p = \frac{1}{(1.58 \times 10^{-7})\left(\frac{1.58 \times 10^{-7}}{2}\right)^{1/2}}, \text{ or } = 2.25 \times 10^{10}.$$

Substituting the values of Baur and Glaessner in this equation,

$$\frac{0.41}{(0.59)(p_{O_2})^{1/2}} = 2.25 \times 10^{10}$$

and therefore, $P_{O_2} = 0.95 \times 10^{-5}$ atmospheres, at 1000° abs.

---

[1] *Publication of the Carnegie Institution*, No. 61; *Z. physik. Chem.*, 58, 334 (1907).

[2] *Z. physik. Chem.*, 43, 358 (1903).

[3] *Ibid.*, 56, 556 (1906).

It is also evident that equilibrium measurements similar to the above, but with carbon present as an additional solid phase, would be equally useful for evaluating the partial pressure of oxygen over ferrous oxide. Such measurements have been carefully made by Schenck, Similler and Falcke.[1] Marked differences in the total pressures were found when different varieties of carbon were used, but the relative amounts of carbon monoxide and dioxide were found to be independent of this factor, as would be expected. Since only these relative amounts of carbon monoxide and dioxide concern us in the present calculation, we can select those measurements made in the immediate vicinity of 1000° abs., which happen to be those where amorphous carbon was used. Interpolating for 1000° we find that the equilibrium mixture contained 61 per cent. carbon monoxide and 39 per cent. carbon dioxide. Substituting these values in the above equation derived from the results of Nernst and v. Wartenberg, we obtain for the partial pressure of oxygen at 1000° abs.

$$P_{O_2} = 0.81 \times 10^{-21}.$$

This agrees excellently with the value 0.95×10^{-21} obtained from the results of Baur and Glaessner. The mean of both results is

$$P_{O_2} = 0.88 \times 10^{-21}.$$

The dissociation pressure of oxygen over the oxide at 25° can be calculated from this value by means of the van't Hoff equation, knowing the heat of formation. We cannot, however, assume that the heat of formation is constant over so long a range, and a modified form of the van't Hoff equation must therefore be used. Such an equation has been deduced by Lewis[2] and applied to a similar problem. It is

$$\ln \frac{p_1}{p_2} = -\frac{U_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{R - C}{R} \ln \frac{T_1}{T_2},$$

where

U_0 = twice the heat of formation of ferrous oxide at absolute zero;
T_1 = 1000° absolute;
T_2 = 298°.
p_1 = the partial pressure of the oxygen at $T_1 = 0.88 \times 10^{-21}$ atm.;
p_2 = the partial pressure of the oxygen at T_2;
C = the decrease in the heat capacity of the system $2FeO = 2Fe + O_2$, when a molecular weight of oxygen is liberated;
R = the gas constant = 1.985 cal./T.

The value of C at 25° can be computed with some accuracy. According to Pionchon's[3] formula, representing his observations below 700°, the specific heat of iron at 25° would be 0.1116 cal./T. Taking Nernst and v. Wartenberg's[1] formula for the molecular heat of permanent gases, based on Holborn and Austin's[2] measurements, the molecular heat of oxygen at constant volume would be 4.76 cal./T. The author and Mr. Barmeyer, in some unpublished measurements of the specific heat of ferrous oxide, found the specific heat of this substance to be 0.1660 cal./T at 25° to 100°, or 0.1627 at 25°, assuming that its specific heat changes at the same rate as does that of iron. Referring these values to equivalent molecular quantities, we find that

---

[1] *Ber.*, 40, 1708 (1907).

[2] *Loc. cit.*

[3] *Ann. chim. phys.*, [6] 11, 72 (1887).

$$\begin{aligned} C_{25} &= 2 \times (11.65) - 4.76 - 2 \times (6.23) \\ &= 6.08 \text{ cals.} \end{aligned}$$

The *mean* value of C over the temperature interval of 25° to 727°, which we require, can not be computed with as much accuracy, for the temperature coefficient of the specific heat of ferrous oxide is not known. An approximate value for C_{mean} can be obtained by assuming that this coefficient has the same relative value as that of metallic iron. Taking Pionchon's measurements at 710° as a basis, we find that 116.9 cal. is required to heat one gram of iron from 25° to 727°, or 13056 cals. for two-gram atoms. A gram molecule of oxygen would require 3400 cals. to be heated through the same interval. Assuming that ferrous oxide has the same temperature coefficient as iron below the recalescent point, two gram molecules of it would require 22,770 cals. It follows then that

$$C_{\text{mean}} = \frac{22770 - 3400 - 13056}{702} = \frac{6317}{702} = 9.0 \frac{\text{cal.}}{\text{T}}.$$

The uncertainty in the assumption regarding the temperature coefficient of the specific heat of ferrous oxide is so great that this value might be in error by as much as one or two calories. This inaccuracy has but a negligible effect on the final result.

The heat of formation of ferrous oxide has been measured directly by Le Chatelier,[3] using a calorimetric bomb. He found it to be 64,600 cal. at 17° and constant volume (for *one* gram molecule). The heat of formation at absolute zero may be found from the expression

$$U_0 = U + CT.$$

Therefore,

$$\begin{aligned} U_0 &= 2 \times (64{,}600) + 6\ (17 + 273) \text{ cal.} \\ &= 130{,}940 \text{ cal.} \end{aligned}$$

Substituting these values in the above equation, we obtain

$$p_2 = P_{O_2} = 4.4 \times 10^{-90} \text{ atmospheres at } 25°.$$

A cell at 25°, consisting of an oxygen electrode and an iron electrode, plunged in a saturated solution of ferrous hydroxide, would then give zero electromotive force when the pressure of the oxygen over the oxygen electrode equaled 4.4×10^{-90} atmospheres.

---

[1] *Loc. cit.*

[2] *Sitzungsber d. kgl. preuss. Akad.*, 1905, p. 175.

[3] *Compt. rend.*, 120, 623 (1895).

One can now calculate from the familiar equation of Nernst what electromotive force such a cell would have if the pressure of the oxygen were increased to atmospheric, and, knowing the solubility of ferrous hydroxide or ferrous oxide, what the electromotive force would be were the iron and hydroxyl ions present in normal concentration. Thus, were the oxygen at atmospheric pressure, the electromotive force would equal

$$E = \frac{0.059}{4} \log \frac{1}{8 \times 10^{-88}} = +1.279 \text{ volts.}$$

The solubility of ferrous hydroxide in water has been determined by Mr. Bridges and the author to be 1.35×10^{-5} mols. at 25°. Then, for the cell

$$\text{Fe/M/1 Fe}^{\cdot\cdot} / 1.35 \times 10^{-5} \text{ M Fe}^{\cdot\cdot} / \text{Fe}$$

$$E = -0.144 \text{ volt,}$$

and for the cell

$$O_2 \text{ atmospheric / M/1 OH}'/2.70 \times 10^{-5} \text{ M OH}'/O_2 \text{ atmospheric,}$$

$$E = +0.269 \text{ volt.}$$

Combining these cells we obtain for the cell

$$\text{Fe / M/1 Fe}^{\cdot\cdot} \text{ / M/1 OH}' / O_2 \text{ atmospheric,}$$

$$E = +0.866 \text{ volt.}$$

Taking the normal calomel electrode as —0.564 at 25°, the potential of oxygen against normal hydroxyl ions is —0.674, according to the recent investigations of Lewis[1] and others.[2] Hence the single potential of iron against a molecular normal solution of ferrous ion would be

$$E = \mathbf{0.192} \text{ volt.}$$

This value agrees excellently with the value 0.19 volt obtained by Richards and Behr.

The significance of this agreement can be determined only by an examination of the experimental data as regards their probable errors, and the effect of these errors upon the final result.

Of these data the one requiring the most careful scrutiny from this point of view is the heat of formation of ferrous oxide. The value 64,600 cal., used in the above calculation for this quantity, was obtained by Le Chatelier from an experiment with a calorimetric bomb. The heat of formation of HYDRATED ferrous oxide calculated from three independent series of experiments[3] has an identical value in each case of 68,300 cal. at room temperature and constant pressure, or 68,000 cal. at room temperature and constant volume. This roughly confirms the value found by Le Chatelier for dry ferrous oxide, as we should expect a higher value for the hydrated form. The difference, however, is greater than the probable heat of hydration, and would indicate that Le Chatelier's value was too low rather than too high.[1]

---

[1] *Z. physik Chem.*, **55**, 465 (1906); THIS JOURNAL, **28**, 130 (1906).

[2] *Z. physik Chem.*, **56**, 513 (1906); *Ibid.*, **59**, 313 (1907).

[3] Andrews, *Pogg. Ann.*, **59**, 439 (1843); Thomsen, *J. prakt. Chem.*, [2] **11**, 419 (1875); Berthelot, *Ann. chim. phys.*, [5] **23**, 118 (1881); see Ostwald, Lehrbuch II^2, 295.

It appears improbable from these considerations that LeChatelier's value is in error (probably low) by more than three per cent. This error would give rise to an error in the potential of iron of about 25 millivolts, and in the sense that a higher value of the heat of formation would give a higher value for the potential.

The other data involved in the calculation afford less probability of error. Thus any considerable error in the value for the partial pressure is unlikely. The partial pressure was calculated from two independent series of observations and the resulting values agreed to within a few per cent. Data on the dissociation of carbon dioxide were involved in both calculations, but their accuracy is well established. It would seem highly improbable that the mean value for the partial pressure could be in error by 100 per cent., but even then the potential of iron would be altered only by seven millivolts.

The solubility measurements were made by the Kohlrausch method and the value employed was the mean of several concordant results. It is improbable that this value is in error by more than ten per cent. An error of this magnitude would only affect the final potential by about three millivolts, and in the sense that an increase in the solubility of the hydroxide would raise the calculated potential.[2]

---

[1] This heat of formation can be roughly calculated directly from the measurements of Baur and Glaessner, for their experiments extended over nearly two hundred degrees. Applying the above combination of van't Hoff's and Kirchhoff's theorems to the experimental values at 727° and 880°, inserting the corresponding values for the dissociation as calculated from the observations of Nernst and v. Wartenberg, and using the same values for the specific heats, we obtain $U_0/2 = 72{,}000$ cal. or $U_{17}/2 = 72{,}870$ cal Or, starting from the fact that the Fe, FeO, CO, CO_2, O_2 equilibrium curve, obtained by Baur and Glaessner, shows a minimum at 680°, and that hence the heat of reaction must be zero at this temperature, we know that there the heat of formation of carbon dioxide from carbon monoxide must equal the heat of formation of ferrous oxide. Using the data collected by Haber (Thermodynamics of Technical Gas Reactions, p. 317), we find this to be 67,490 cal Correcting this to 17°, using the same specific heat as above, we obtain $U_{17}/2 = 70{,}470$ cal The accuracy of Baur and Glaessner's measurements is not, however, sufficient for calculations of this sort—and the values here given may well be in error on that account by 10 per cent. They can do no more than roughly indicate that the heat of formation of ferrous oxide at high temperatures is the same as that at low temperatures, and that LeChatelier's value for the heat of formation is perhaps too small.

[2] The uncertainty regarding the specific heat of ferrous oxide is of very slight importance in the calculation of the potential. An error of 50 per cent. in it would only affect the potential by about three millivolts. There is a slight error involved in taking the solubility of the ferrous hydroxide instead of that of ferrous oxide. The

Summarizing this calculation of the potential of iron and this discussion of the effect of the probable experimental errors on the final result, we may say:

(1) That the calculated potential of iron against a molecular normal solution of ferrous ions, taking the calomel electrode as —0.564 volt, is 0.192, in excellent agreement with the experimental results of Richards and Behr;

(2) That, in so far as errors in the experimental data involved are concerned, this result can scarcely be in error by more than three centivolts, and that it is probably too low, rather than too high.

UNIVERSITY HEIGHTS, NEW YORK CITY,
June 20, 1910.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE.]

THE INVERSION OF CANE SUGAR BY INVERTASE. VI. A THEORY OF THE INFLUENCE OF ACIDS AND ALKALIS ON THE ACTIVITY OF INVERTASE.

BY C. S. HUDSON.

Received July 9, 1910.

In alkaline solutions invertase shows no activity, in weakly acid solutions its enzymotic power reaches a maximum from which it decreases with increasing acidity. The simplest theoretical interpretation of this striking fact is that acids and alkalis combine with invertase by the principles of the law of mass action and prevent it from inverting cane sugar. In the following calculations this hypothesis will be tested. If invertase combines with both acids and alkalis it is an amphoteric electrolyte and may be assumed to dissociate as follows:

(1) Invertase $\rightleftarrows \dot{H}$ + anion (acidic dissociation).

(2) Invertase $\rightleftarrows OH'$ + cation (basic dissociation).

If a units of invertase are dissolved in a unit volume of a solution containing hydrogen and hydroxyl ions in the fixed concentrations $(\dot{H})$ and (OH), it will form x units of anion and y units of cation, leaving $a - x - y$ units of undissociated invertase. The mass-action law requires the fulfilment of the following conditions when equilibrium is attained:

$$(3)\ \frac{(x)(\dot{H})}{(a-x-y)} = K_1, \text{ and } (4)\ \frac{(y)(OH')}{(a-x-y)} = K_2$$

The quantity $a - x - y$ is the concentration of uncombined or undissociated invertase, and it is here assumed that the enzymotic activity is caused by this substance and is proportional to its concentration.

---

difference, however, must be small, since, from the properties of ferrous oxide, we know that the heat of hydration is probably very small. Since the solubility of ferrous oxide, could it be measured, would be greater than that of ferrous hydroxide, this inaccuracy also tends to make the true potential higher.

Solving (3) and (4) for $a - x - y$ gives

$$\text{Activity } (i.\ e., a - x - y) = \frac{a}{1 + \frac{K_2(\dot{H})}{K_w} + \frac{K_1}{(\dot{H})}}. \quad (5)$$

where K_w is the dissociation constant for water. This formula contains the three coefficients a, K_1, and K_2, which are of unknown values; in order to determine the values of these coefficients the data which were found for the activity of invertase in three solutions containing small concentrations of hydrochloric acid are used, namely:[1]

HCl concentration Normal	Activity of invertase
0 0005	62
0 0015	61
0 008	37

These data when introduced in equation (5) give the values $a = 77$, $K_2/K_w = 133$, and $K_1 = 0.000086$, and formula (5) becomes

$$\text{Activity} = \frac{77}{1 + 133\,(\dot{H}) + \frac{0.000086}{\dot{H}}}. \quad (6)$$

From this formula the activities of invertase over a considerable range of acidity and alkalinity have been calculated and are recorded in Table I in comparison with the activities which were found experimentally

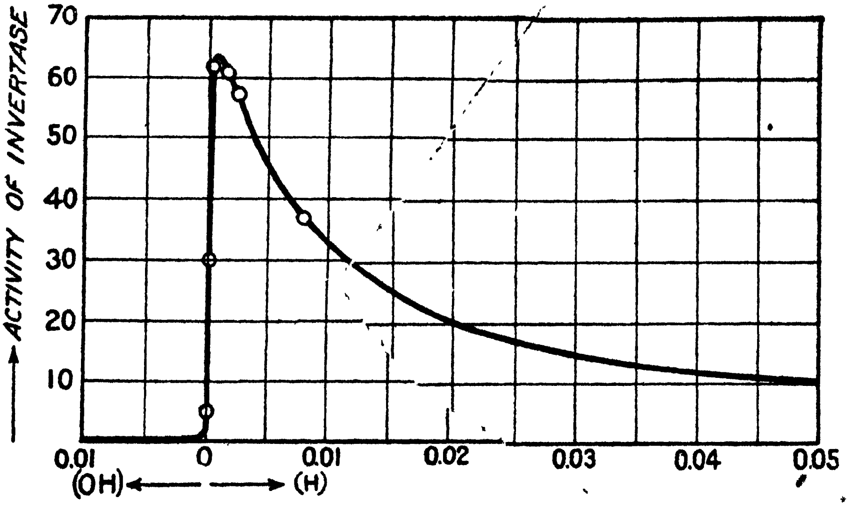
TABLE I.—CALCULATED AND OBSERVED ACTIVITIES OF INVERTASE.

HCl concentration.	Calculated activity	Observed activity.
$(10)^{-8}$ (alkaline)	0.001	0 0
$(10)^{-7}$ (pure water)	0.1	5.0
$(10)^{-6}$	0.9	. . .
$(10)^{-5}$	8.0	. . . .
0.00009	39	30
0 0005	(62)	(62)
0.0015	(61)	(61)
0.002	59	. . . .
0.003	58	58
0.005	45	. . . .
0.008	(37)	(37)
0.01	33	. . . .
0.02	21	. . . .
0.03	15	. . . .
0.05	10	. . . .

By reference to the figure it will be seen that there is a remarkably close agreement between the calculated and observed activities: the calculated values are shown by the smooth curve, the observed activities by the circles. On account of the rapid destruction of invertase at 30° by acid above 0.01 normal the relation can not well be tested beyond that concentration, but it is probable that at 0° such measurements can be made, and this will be attempted in the near future.

---

[1] THIS JOURNAL, 32, 777. In line 7 of the page referred to, the word printed "acidity" should be "activity."



Graph of the formula for the activity of invertase.

The concentration of acid for which the enzymatic activity is a maximum can be calculated from equation (5). Writing its first differential with respect to $(\dot{H})$ equal to zero and solving gives

$$(\dot{H})_{\max} = \sqrt{\frac{K_1 K_w}{K_2}}. \qquad (7)$$

Substituting in this the values previously found for these constants gives $(\dot{H})_{\max} = 0.8(10)^{-3}$ at 30°. Sörensen,[1] from his experiments at 52°, has found this value to be approximately $(10)^{-4}$; our results are thus in fair agreement with his, but they can not be strictly compared because of the different temperatures used, namely, 52° and 32°.

[Contribution from the John Harrison Laboratory of Chemistry.]

METALLIC STRONTIUM.[2]

By Ben L. Glascock.

Received July 23, 1910.

In no case has strontium been obtained in sufficient amount to admit of a thorough study of its properties. The most complete investigation thus far has been that of Guntz and Roederer,[1] who prepared the metal from its hydride, made from the amalgam.

---

[1] *Comptes rendus des travaux du Laboratoire de Carlsberg*, **8**, 132 (1909).

[2] From the author's doctoral thesis, 1909.

The purpose of the present investigation was to develop, if possible, a process or [illegible] metal could be obtained in sufficiently [illegible] study of its properties. The electrolysis [illegible] he most promising solution. It had been [illegible] and Matthiessen and by Stockem and [illegible] could be made in this way. The problem resolved itself, then, into devising an improved or simpler form of apparatus, or a change in the electrical conditions.

The objection to the method of Bunsen and Matthiessen[3] is that with external heat, in addition to that afforded by the passage of the current, it is exceedingly difficult to regulate the temperature of the furnace so that a crust of chilled strontium chloride will always cover the bath in the inner cell. Stockem and Borchers avoided this difficulty by collecting the metal at the bottom of the bath. They found that the metal did not combine with the strontium chloride to such an extent as to render their method a failure. They cooled the bottom of the furnace, however, by means of a water jacket. The furnace of these workers is complicated, necessitating, as it does, the use of heavy insulation between the poles, a threaded point or rod for the cathode, and a water jacket for cooling purposes, all of which rendered the apparatus difficult of construction.

The method of Goodwin[4] for the preparation of calcium suggested itself as a possibility for strontium. To test it, a furnace was constructed by firmly binding together four Acheson graphite blocks by means of four heavy iron straps and bolts. The dimensions of the blocks were 10 cm. × 10 cm. × 30 cm. The two upper blocks had two semicircular sections sawed from them in such a way and of such a size that when they were fitted together they formed two holes 10 cm. deep, one 7.5 cm. in diameter, the other 10 cm. These holes fitted directly over depressions in the lower set of blocks, made by chipping out the graphite. Asbestos paper was put in between the blocks and the whole tightly bound together by means of the straps and bolts. The use of the asbestos was to prevent leaks, not to serve as insulation. The furnace was then connected to the + terminal of the feed wires by means of one of the bolts; thus all four blocks were connected with the current. An iron rod 2 cm. in diameter attached to the ratchet device used in the Goodwin furnace and connected to the — terminal served as the cathode. The circuit carried a 500-ampere ammeter and a 110-volt voltmeter, and a wooden barrel rheostat. The electrodes in the barrel were ordinary slabs of scrap iron, one of which could be lowered or raised by means of a cord passing over a pulley. If such a furnace would serve for the preparation of calcium it would be an improvement over the more or less fragile and complicated furnace of Goodwin, in that it could be taken apart entirely and the chilled calcium chloride left after the run easily removed, and in that it would do away with the use of the water-cooling apparatus, the graphite blocks being massive enough to conduct the heat away as rapidly as the water coil would, and also in that it would do away with the "gravity" cell of his furnace.

---

[1] *Compt. rend.*, 143, 400–1.

[2] *Elec. Metallurgie*, Borchers, p. 84.

[3] *J. prakt. Chem.*, 107, 253 (1869).

[4] THIS JOURNAL, 27, 1403.

To try out the furnace, one of the holes was filled with melted calcium chloride, which had been fused in an iron dish in a wind furnace, the cathode lowered into the bath and the current switched on. Metallic calcium began at once to form on the iron, and rods of the metal as much as twenty inches in length were easily drawn out by means of the ratchet device. Each of the holes or furnaces were tried repeatedly. Each gave the same satisfactory results—they had equal efficiency. By repeated trials with varying current, it was found that about 80 amperes and 40–50 volts gave the best results with this apparatus This, of course, is a matter that is entirely dependent upon the size and depth of the bath. The furnace, when full, contained enough calcium chloride to last six to eight hours with the above current, the yield in metal being in the neighborhood of 300 grams. As the object of these experiments was merely to show whether or not the furnace could be used successfully for calcium, no careful measurements or weights were taken with a view of ascertaining the efficiency of the apparatus. No inconvenience whatever was caused by leakage. Occasionally, however, a superficial lining of calcium fluoride was put into the furnace as an additional safeguard.

The Preparation of Metallic Strontium.

The apparatus described above was used with strontium chloride as the electrolyte, but metallic strontium was never obtained. It was impossible to prevent its burning and its combination with the electrolyte. It would not adhere to the cathode and thus become protected by a layer of strontium chloride, as is calcium in its preparation from calcium chloride. This may be due partly to the fact that it is less stable in the air than calcium is, and partly to the higher temperature of the electrolyte.

A cathode 6 cm. in diameter was substituted for the smaller one, and the current was just sufficient to keep the electrolyte molten. A layer of strontium chloride mixed with a small amount of metal was found to cover the end of the iron. A considerable quantity of hydrogen was evolved when th [illegible] re was thrown into water. Three trials were made with [illegible] ith the same result.

A [illegible] bout 0.3 cm. in diameter, was next tried. The [illegible] hat the intense heat in the immediate vicinity [illegible] cause the liberated metal to fuse into globules [illegible] mitting their removal. After electrolyzing for 4–5 hours, [illegible] urrent sufficient to keep the whole bath molten, the cathode [illegible] removed. No strontium was attached to it, nor were globules of the metal observed on the surface of the bath at any time during the operation. There seemed, however, to be less burning than usual. When the cold mass was broken open, it was found to be full of violet colored spots or nodules. These nodules gave considerable hydrogen when thrown into water. The experiment was repeated several times, but the results were never different.

It was thought perhaps metal could be obtained if the temperature of the electrolyte were lowered. For this purpose baths of strontium chloride with varying amounts of strontium fluoride were used. The cathode was the same as that used for calcium—2 cm. in diameter. When an electrolyte of strontium chloride and 10–20 per cent. of strontium fluoride with a current of 140–150 amperes and 20–30 volts was employed, globules of metal formed and floated about on the surface of the bath. Several of these were taken out, but they ignited at once, burning energetically with an intensely red flame. When the burning metal was thrown on the floor it broke into pieces and flew in all directions, tracing figures, as calcium or antimony does under similar conditions. When the cathode was removed, it was found to be covered with a layer of strontium chloride about 0.6 cm. in thickness, which contained so much metal that pieces of it glowed when struck violently with a hammer, and caused a brisk evolution of hydrogen when thrown into water. If a less powerful current was used, the metal burned as fast as it was formed, and if the current was allowed to fall after the metal began to separate, the globules were seen to glow and to gradually disappear.

When a bath of strontium chloride and about 50 per cent. of strontium fluoride with a current of 125 amperes and 40 volts was employed, it was noticed that small glowing particles were distributed through the mass, and they seemed to fall slowly to the bottom. Upon removing the cold material from the furnace, a thin black layer covered the bottom of it. It contained considerable metal and carbide.

This observation led to the next logical step—a reversal of the poles. This was done by placing a strip of sheet iron between the upper and lower sets of carbon, thus forming, at once, the cathode and the bottom of the furnace. A thick piece of asbestos with a hole in it to fit the furnace was laid over the iron and the whole apparatus bound together as before, after the upper set of blocks ha[illegible] been separated from the iron straps and bolts by thick pieces of asb[illegible] carbon rod 2.5 cm. in diameter served as anode. In other w[illegible]ace of Stockem and Borchers had been arrived at, but in a m[illegible]n.

Using this furnace with the bath last described a[illegible]o amperes and 70–80 volts for three hours, a layer was formed [illegible] which contained considerable metal and carbide. The metal [illegible] in globules. With a bath of strontium chloride and 25 per cent. of stron-tium fluoride and a current of 50–60 amperes and 50–60 volts for four hours a layer was obtained next to the cathode, which, in places, contained so much metal that when it was scratched, the whole took on a metallic luster. This, of course, soon disappeared because of the instability of the metal in air. It decomposed water energetically.

A bath consisting of strontium chloride and 10 per cent. of strontium fluoride was next used. The current was passed for $7^1/_2$ hours. About half the time it registered 150 amperes and 20 volts, the other half 60 amperes and 50 volts.[1] When the cold mass was broken open, it showed globules of metallic strontium. Many of the pieces were as large as a pea. Fourteen grams of the metal were separated. In addition to the metal several nodules of a brilliant yellow substance were found. This was very brittle, and was rather stable in the air; when put into water an energetic evolution of acetylene occurred.

The experiment was repeated, with like results.

An attempt was made to fuse together the pieces of metal that were too small to be separated mechanically. The residue was put into a 2.5 cm. gas pipe, capped at the ends, and placed in a vertical position in a wind furnace. The strontium alloyed with the iron and holes appeared in the cap and pipe, although the temperature was much below that of the melting point of iron.

The preceding experiences having demonstrated that any contrivance for cooling the furnace was unnecessary, it was decided to resort to an even simpler form of apparatus. To this end a cast iron vessel of hemispherical shape 25 cm. in diameter and walls 0.6 cm. in thickness was made to serve as a container. To keep the liberated metal from contact with the air and also to carry out Stockem and Borcher's idea of a small cathode, an iron rod 1.8 cm. in diameter, bent at right angles about two inches from its lower end, and this end then hammered to a blunt point, was made to serve as the cathode. A carbon rod 2.5 cm. in diameter was used as anode. By this arrangement, the current was made to pass entirely beneath the surface of the bath, since the vessel was deep enough to prevent the current passing to it and thence to the other electrode. It also admitted of the use of a porous cell arrangement—Bunsen and Matthiessen's idea.

---

[1] During this electrolysis the carbons of the furnace attained a red heat throughout. This would indicate that a water jacket is entirely unnecessary, since the metal had been obtained under these conditions.

The vessel was filled with fused strontium chloride, the current switched on, and a porous plate interposed. The same bath was used on three different days, connection being established by drawing an arc from the iron cathode upon the anode by means of a thin carbon rod held in the hand until the electrolyte was sufficiently fused to carry the current. During the electrolysis the bath in the vicinity of the cathode was always covered with a crust of chilled chloride. A very small amount of metal was seen to burn, but when the mass was broken up after the third day, only about 1 gram of metal was found.[1]

In the next experiment the dish was made to serve both as container and cathode, the anode remaining the same. Pure strontium chloride was used as the electrolyte. A current of 75 amperes and 75 volts was passed for $3^1/_2$ hours. Fifteen grams of metal were obtained. There was a noticeable decrease in the amount of carbide observed. The globules were larger than heretofore. The mass was re-fused and a current of 75 amperes and 75 volts passed for eight hours. Toward the end of the electrolysis, globules of metal were seen to come to the surface and float to the edge of the dish and either burn there or sink. Efforts to remove these globules were not very successful. When the bottom of the electrolyte was disturbed by scraping it with a rod, large pieces of metal would rise to the surface, showing the presence of considerable strontium.

It was thought that the metal could be made to run into one large piece, if the vessel and its contents were heated in a wind furnace. This was done. The strontium alloyed with the iron, however, produced a large hole in the bottom of the dish. The temperature was far below the melting point of iron. The iron in the vicinity of the hole was very soft, almost plastic, at low red heat. When cold it was hard and brittle, and had a different fracture from cast iron. A small amount of hydrogen was given off when it was boiled with water. Some of the metal was thoroughly washed, dissolved in hydrochloric acid, the solution filtered from the insoluble matter, and sulphuric acid and alcohol added to the filtrate. A heavy precipitate formed at once. Enough strontium was present to give a dense precipitate with sulphuric acid even in the absence of alcohol.

An iron mortar 15 cm. in diameter at the top and 15 cm. high, having a capacity of 1 liter, was substituted for the iron vessel just described. A current of 45 amperes and 75 volts for 8 hours gave about 7 grams of material which contained enough metal to render it malleable. Repeated trials failed to give any better results. The vessel was too small.

---

[1] A very interesting observation was made at this point. When the residue was put into water, preparatory to recovering strontium chloride, a vigorous evolution of acetylene and ammonia took place. The odor of phenyl isocyanide was also detected. The greater portion of the carbon from the anode, however, remained as carbon when the residue was leached out with water.

Another cast iron vessel of the same dimensions as the first one was procured. A carbon anode 8 cm. × 8 cm. was substituted for the smaller one. This large carbon permitted the use of a lower current density at the anode, thus reducing the temperature of the bath. With an electrolyte of pure strontium chloride and a current of 125 amperes and 40 volts for 7 hours, 76 grams of metallic strontium were obtained, giving a current efficiency of 5.3 per cent. One piece of the metal weighed 8 grams and several as much as 3 grams. This was the best yield obtained, but 30 to 50 grams were easily isolated by duplicating the above conditions. In all 360 grams of metallic strontium were made with this apparatus, which is extremely simple and involves the use of no expensive material. It was found that passing the current longer than 6–8 hours decreased the actual yield, the best percentage yield being when a current of 135 amperes and 35 volts was passed for only two hours. 29.5 grams of metal were isolated, or a current efficiency of 6.7 per cent. was attained.

Vessels and anodes of varying size and electrolytes of varying composition were tried out, but the conditions previously mentioned gave the best results.

The best method for separating the metal from the mixture consists in crushing it on an ordinary iron plate, then sieving out the metal.

Some very interesting phenomena and products revealed themselves during the process of recovering the strontium chloride from the melts. When the melt from the pure strontium chloride bath was extracted with water, there remained a residue which was soluble in hot water. Upon cooling this solution crystals separated. They had an alkaline reaction and all the properties of strontium hydroxide.

Upon concentrating the mother liquor from these crystals, it took on a pink color, which grew more intense as the concentration proceeded. The solution was alkaline. On addition of acid the color changed to light yellow. Bases restored the pink color. This product was obtained repeatedly, but never in amounts large enough to permit of the determination of its constitution.

To remove the iron salts from the first water extract, containing most of the strontium chloride, the solution was evaporated to dryness with a small amount of nitric acid and then baked, the residue extracted with water, and the extract made ammoniacal. The ammonium hydroxide instead of giving a red-brown precipitate of ferric hydroxide gave a voluminous white precipitate that resembled aluminium hydroxide.

Examination showed that it was neither an aluminium nor a titanium compound.

When the solution was evaporated to dryness without the addition of nitric acid, a blue tint would often appear around the edges of the residue, suggesting the presence of cyanide in the solution.

Properties of Metallic Strontium.

Strontium is a very light, soft metal of a silver luster when a new surface is first exposed; this, however, rapidly changes to a yellowish tint and finally to a white non-lustrous surface as the layer of oxide forms over it. It is harder than sodium but softer than calcium; it can be cut easily with a knife. It reacts with water, with methyl and ethyl alcohols, acetoacetic and malonic esters, and aniline with the evolution of hydrogen. It reacts slowly with ethyl iodide at the boiling point of the latter. It has no action upon silicon tetrachloride in either the hot or cold condition. It alloys with iron, and seems to combine with amorphous chromium and boron when heated with them. It dissolves very easily in liquid ammonia, giving a deep blue solution from which a dark blue precipitate separates as more metal dissolves. As the ammonia evaporates from this precipitate it passes through the beautiful play of colors that a clean sheet of copper shows as it cools after being heated to a high temperature, finally exhibiting a bright bronze luster and passing into a white compound as all the ammonia evaporates. Strontium burns in an atmosphere of carbon dioxide and illuminating gas as energetically as it does in air, but not so violently as calcium does under similar conditions. Carbon is set free and some carbide is formed when it burns in the former. Hydrogen and nitrogen unite with the heated metal when they are passed over it, forming the hydride and nitride, respectively. The hydride reacts more energetically with water and alcohol than the metal does.

On analysis three different samples of the metal gave the following results:

	I	II.	III.
Insoluble	0.04	0 04	0.92
$Fe_2O_3(Al_2O_3)$	0.14	0.02	
Sr	97 11	98.50	98.54
Ca	...	...	None
Mg	...	...	None
Cl	1.75	...	...
O (by difference)	0.96	...	...
	100.00		

The specific gravity of strontium determined in dry toluene in a 50 cc. pycnometer gave the value 2.55.

The specific heat of the metal, determined in an ordinary water calorimeter, by putting a weighed amount of the metal into an ordinary test tube, covering it with a weighed quantity of dry toluene, and then the tube sealed off as near the surface of the liquid as possible, gave the following results after corrections had been made for the toluene and glass by means of a blank:

$$\left.\begin{array}{l}0.0779\\0.0701\\0.0736\\0.0757\\0.0771\\0.0681\\0.0768\end{array}\right\}\text{average, } 0.0742$$

This value multiplied by the atomic weight of strontium gives 6.5 as Dulong and Petit's constant.

Alloys.

Various alloys of strontium have been described. Willner[1] has made and analyzed alloys of strontium with tin, magnesium and aluminium.

An alloy of iron and strontium has not been mentioned in the literature. Such an alloy made in an accidental way has been noted in the first part of this communication. Hirsch and Aston[2] have shown that pressure is necessary for the alloying of calcium and iron. It was thought that strontium and iron would unite at atmospheric pressure. To test this assumption some iron, reduced by hydrogen (90 per cent.), was put into a hard glass tube, a few pieces of strontium placed on top of it, and the whole covered with iron. The tube was drawn down to a capillary and then sealed off, when the end containing the mixture was heated to low redness. It was then heated in a good blast lamp. When the fusion point of glass was reached the sides of the tube just above the iron fell inward; heat was applied until the glass began to be blown outward. When a bright red heat was reached, portions of the contents were seen to glow. Upon breaking open the tube, a lump of rather hard metallic alloy was found inside. On filing, it presented a bright homogeneous metallic surface; the luster soon disappeared, however. The alloy decomposed water readily. On analysis it gave:

	Per cent.
Insoluble	0.32
Iron	70.14
Strontium	22.95

An alloy was made by fusing iron by hydrogen in the electric furnace and then plunging strontium into the molten mass. A better one, however, was obtained, by plunging the metal into molten cast iron. Each slowly evolved hydrogen from water.

PHILADELPHIA, PA.

---

[1] Dissertation, Freidrich Wilhelm Universität, Z. Berlin, 1907.

[2] *Proc. Am. Electro-chem. Soc.*, 13, 143.

THE RAPID DETERMINATION OF COPPER, SILVER, CADMIUM AND BISMUTH BY MEANS OF THE MERCURY CATHODE AND STATIONARY ANODE.

By R. C. Benner

Received July 11, 1910

In the search for rapid methods in electrochemical analysis, all desire for simplicity seems to have departed. Various means have been used to agitate the electrolyte. The rotation of the anode or cathode by mechanical means, the use of a solenoid, and the passing of a gas through it have all been tried, but not until recently has any one thought that the evolution of the gas by the electrolytic current might stir the electrolyte sufficiently to allow the metals to be deposited in an adherent and weighable form. This has been done by Stoddard,[1] Frary[2] and the author[3] with the gauze electrode, in case of copper. It has been shown qualitatively by Stoddard[4] with the mercury cathode and stationary anode, for copper, silver, etc.

In both cases the current densities are higher than ordinarily used with stationary electrodes. With the gauze electrode of the author's there was used a current density of 10 amperes for every 100 square centimeters, and in case of the mercury cathode made use of in this work, a normal density of 35 to 40 amperes. This proves that the rate of deposition in a weighable form must be due, at least in part, to the stirring of the electrolyte by means of the liberated gas.

Therefore, in order to determine whether the evolution of gas would stir the liquid sufficiently to allow complete deposition to take place rapidly and in a weighable form, higher current densities than had been used before for this purpose, were utilized in carrying out the determination of several metals by means of the mercury cathode and a stationary anode.

In order to avoid all danger of loss by the rapid evolution of gas by high currents, taller electrodes than used by Smith were constructed. When these contained 40 to 50 grams of mercury, they did not overload the balance. The mercury used in these determinations was distilled and purified by the method of Hillebrand each time before using. In each case, after the deposition in question was complete, the mercury was washed with distilled water until the current dropped to zero. The current was then broken, leaving the beaker full of water and the anode examined for small globules of mercury by means of a magnifying glass. Mercury was frequently carried to the anode, either by washing or by the rapid evolution of gas from the cathode but could usually be removed by rinsing the anode up and down in the water contained in the beaker. After the anode had been freed from mercury, the water was either poured or siphoned off and the last part removed by means of a capillary tube. The cathode was then washed with absolute alcohol, the greater portion poured off, the last part being removed by the capillary tube. Finally it was washed with ether, the greater portion poured off and the remainder allowed to evaporate. The electrode was placed in a desiccator for one-half an hour. The removal of the last of the water by means of a siphon with a capillary end makes one washing with alcohol and one with ether sufficient.

---

[1] This Journal, 31, 385 (1909).

[2] May meeting of the American Electrochemical Society.

[3] *J. Ind. Eng. Chem.*, 2, 348.

[4] *Loc. cit.*

Copper.—Copper, being one of the easiest metals to determine electrolytically, with accuracy, under the most varied conditions, was selected for the preliminary work. To carry out these experiments, two solutions of nitrate were prepared by dissolving weighed amounts of chemically pure copper foil in the smallest possible amount of nitric acid, diluting to a definite volume with water and checking the copper content by electrolysis with platinum electrodes. The two solutions contained respectively 0.3731 and 0.1912 gram of copper in ten cubic centimeters.

The solutions were electrolyzed with currents varying from three to four amperes in 20 cc. of solution, both sulphuric and nitric acid solutions being used.

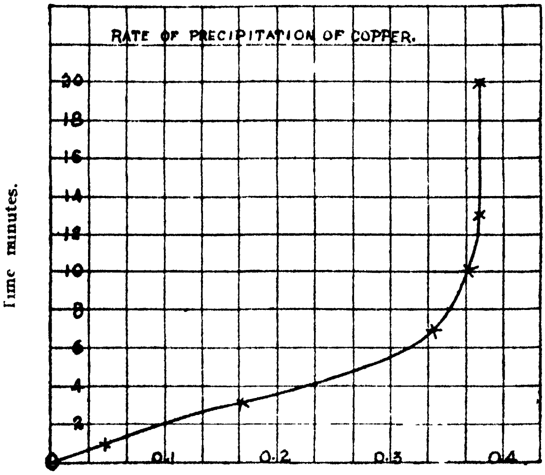
Amount of copper.						
Taken	Found.	Error.	Amperes.	Volts.	Volume of the solution.	Acid, 4 drops
0.3831	0.3835	0.0004	3–4	6–8	20 cc.	H_2SO_4
0.3831	0.3837	0.0006	3–4	6–8	20 cc.	no acid
0.3831	0.3832	0.0001	3–4	6–8	20 cc.	no acid
0.3831	0.3834	0.0003	3–4	6–8	20 cc.	4 drops nitric
0.3831	0.3831	0.0000	3–4	6–8	20 cc.	4 " "
0.1912	0.1919	0.0007	3–4	6–8	20 cc.	4 " "
0.1912	0.1911	0.0001	3–4	6–8	20 cc.	4 " H_2SO_4
0.1912	0.1913	0.0001	3–4	6–8	20 cc.	4 " "
0.1912	0.1906	0.0006	3–4	6–8	20 cc.	no acid
0.1912	0.1910	0.0002	3–4	6–8	20 cc.	no acid
0.1912	0.1912	0.0000	3–4	6–8	20 cc.	no acid

Rate of Precipitation.

In the determination of the rate of precipitation, 20 cubic centimeters of solution were electrolyzed, with a current of four amperes and six to seven volts, in the presence of four drops of concentrated nitric acid.

Time min	Amount of copper.		
	Taken.	Found.	
1	0.3831	0.0535	
3	0.3831	0.1767	
7	0.3831	0.3485	
10	0.3831	0.3782	
15	0.3831	0.3827	
20	0.3831	0.3833	Copper all out.

Examination of the preceding determinations shows that the results were equally good under any of the conditions used, being as accurate as those obtained with the rotating anode and mercury cathode. The precipitation was not as rapid in this case as where the electrolyte was agitated by mechanical means. This was more than compensated for, however, by the simplicity of the apparatus and was not enough slower to be detrimental to the use of this method. It was possible, in 20 minutes, with a current of four amperes, to precipitate 0.3833 gram of copper from 20 cubic centimeters of solution containing four drops of concentrated nitric acid. It has been observed that a black deposit, which was taken to be the peroxide, formed on the anode but redissolved as the electrolysis neared completion. The copper amalgam was washed without delay as soon as the electrolysis was complete, as oxidation takes place readily.



Weights of copper deposited.

Silver.—Silver, as well as copper, is easily and accurately determined by all electrolytic methods. To carry out the experimental work on silver, a solution was prepared by dissolving a weighed amount of chemically pure silver foil in the smallest possible amount of nitric acid and diluting to a definite volume. Ten cubic centimeters of this solution

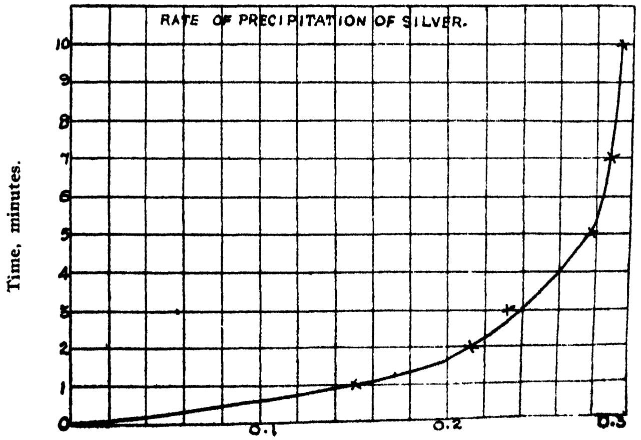
Silver present.	Silver found.	Error.	Acid	Amperes	Volts.
0.1428	0.1430	0.0002	None	4-5	7-8
0.2856	0.2862	0.0006	"	4-5	7-8
0.1428	0.1427	0.0001	5 drops H_2SO_4	4-5	7-8
0.1428	0.1425	0.0003	"	4-5	7-8
0.1428	0.1425	0.0003	4 drops HNO_3	4-5	7-8
0.2141	0.2147	0.0006	"	3-4	4-5
0.2141	0.2146	0.0005	4 drops H_2SO_4	3-4	4-5

contained 0.1428 gram of silver. The solution was then electrolyzed under the same conditions as copper with the additional trial of several organic acids.

Rate of Precipitation.—In order to determine the rate of precipitation 20 cc. of the solution were electrolyzed with a current of four amperes and six to seven volts in the presence of about one drop of nitric acid.

Time.	Amount of copper taken.	Copper precipitated	
1	0.2856	0.1534	
2	0 2856	0.2167	
3	0.2856	0 2300	
5	0.2856	0 2790	
7	0.2856	0.2841	
10	0.2856	0 2862	Silver all out.

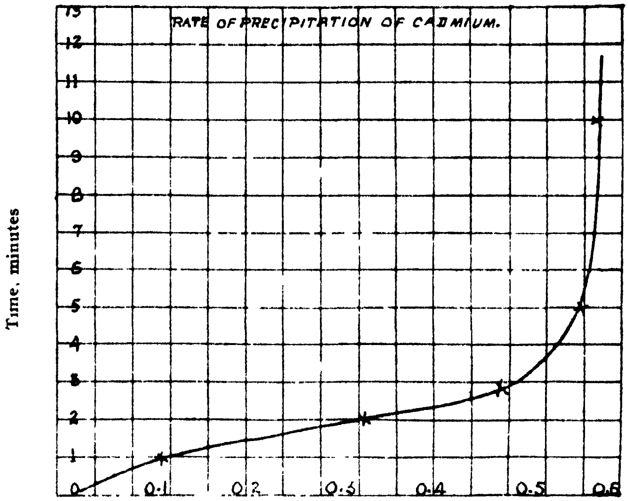
Examination of these results shows them to be comparable in every way with those obtained by means of the rotating anode and mercury cathode. It was possible to deposit 0.2862 gram of silver in ten minutes.



Weights of silver deposited

Large amounts of mineral acids retard the rate of precipitation and give irregular results. All but about one in every ten are low. Citric, tartaric, oxalic and acetic acids were used with results similar to those obtained with large amounts of mineral acids.

Cadmium.—While cadmium has been accurately determined by means of the rotating anode and mercury cathode, it may also be determined by the method used for copper and silver with equally good results. A standard solution was made by dissolving chemically pure cadmium sulphate in water. The cadmium content was found, by the ordinary electrolytic method, to be 0.4828 gram of the metal in 10 cc. This solution was electrolyzed in the usual manner, both hot and cold, with equal success, as will be seen by consulting the following results. It was possible to precipitate 0.5743 gram of the metal in the short period of ten minutes.



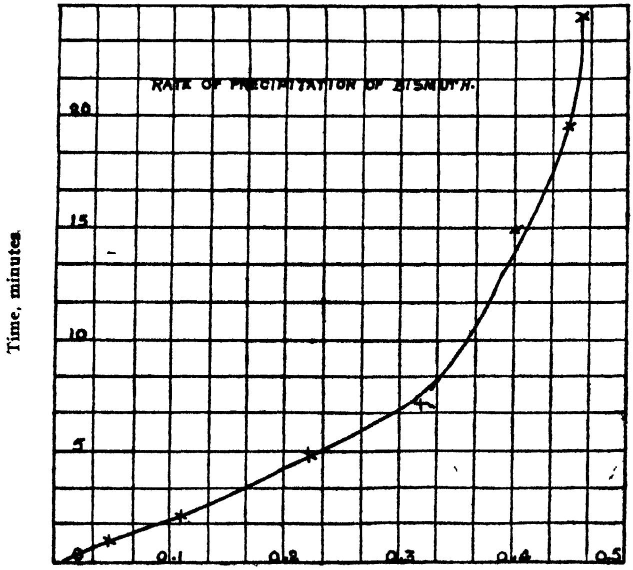
Weights of cadmium deposited

Amount of cadmium.							Volume.	
Taken	Found	Error	Amperes	Volts.	Time	Acid.	Temp	Soln
0 4828	0 4821	0.0007	3-4	7-8	15	4 drops HNO_3	hot	20 cc
0 4828	0 4819	0 0009	3-4	7-8	15	"	cold	20 cc.
0 4826	0 4834	0 0006	3-4	7-8	20	no acid	hot	20 cc.
0 9656	0 9649	0 0007	3-4	7-8	20	4 drops HNO_3	"	20 cc
0 4828	0 4832	0 0004	3-4	7-8	15	"	cold	20 cc.
0 9656	0.9660	0 0004	3-4	7-8	20	"	"	20 cc.
0 4828	0 4836	0.0008	3-4	7-8	20	"	"	20 cc.
0 9656	0 9651	0.0005	3-4	7-8	20	4 drops H_2SO_4	"	20 cc.
0.4828	0 9635	0 0003	3-4	7-8	20	"	"	20 cc.

The rate of precipitation was determined with a current of four amperes and seven to eight volts, in the presence of five drops of concentrated sulphuric acid in 20 cc. of solution.

Time	Amount of cadmium taken.	Amount of cadmium found.	
1	0.5743	0.1131	
2	0.5743	0 3339	
3	0.5743	0.4783	
5	0.5743	0.5566	
10	0.5743	0.5743	Cadmium all out.

Most methods for the determination of bismuth are far from satisfactory. This is true of most electrolytic, as well as of the common analytical methods. In the electrolytic methods the range of conditions for quantitative deposition of the metal in a weighable form is, as a rule, small, and must be strictly observed to obtain the best results. The best and most consistent results are obtained by the use of the mercury cathode, and rapid deposition may also be obtained by combining this with the rotating anode. In order that the rapid determination of this metal might be tried with the stationary anode and mercury cathode, a standard solution of bismuth was made by dissolving some chemically pure bismuth trioxide in the smallest amount of nitric acid which will hold the bismuth in solution when diluted to one liter with water. The amount of bismuth contained in 10 cc. of the solution was determined by precipitating with ammonium carbonate, igniting and weighing as the oxide. The electrolytic determinations were made under the usual conditions in the presence of varying amounts of acid, both nitric and sulphuric acids being used with equally good results, as will be seen by reference to the following table.



Weights of bismuth deposited.

Bismuth present.	Bismuth found.	Error.	Amperes.	Volts.	Time.	Acid added.
0.4650	0.4647	0.0003	3-4	6-7	20-30	none
0.4650	0.4649	0.0001	3-4	6-7	20-30	"
0.2325	0.2326	0.0001	3-4	6-7	20-30	1 cc. of HNO_3
0.2325	0.2325	0.0000	3-4	6-7	20-30	"
0.2325	0.2331	0.0006	3-4	6-7	20-30	½ cc. of H_2SO_4
0.2325	0.2327	0.0002	3-4	6-7	20-30	½ cc. of H_2SO_4
0.4650	0.4655	0.0005	3-4	6-7	20-30	none
0.4650	0.4658	0.0008	3-4	6-7	20-30	"

The original solution contained 0.85 cc. of concentrated nitric acid to every 10 cc. of solution.

The rate at which bismuth was precipitated was determined with 20 cc. of the solution containing 0.4650 gram of bismuth in the presence of 1.20 cc. of concentrated nitric acid.

Time.		Bismuth taken.	Bismuth found.
1		0.4650	0.0510
3		0.4650	0.1100
5		0.4650	0.2263
7		0.4650	0.3244
10		0.4650	0 3622
15		0.4650	0.4027
20		0.4650	0.4528
25	Bismuth all out.	0.4650	0.4645

During the electrolysis, what was taken to be the peroxide always collected on the anode, but, as in other cases, it always dissolved without any trouble before the determination was complete. The smaller the amount of acid present the more likely this was to form. In one or two cases small amounts of the oxide did not dissolve from the anode where it was rough but the amount was not weighable. A black precipitate of bismuth frequently collected under the anode on the mercury but as the electrolysis proceeded this amalgamated without difficulty. It was possible to precipitate, by means of this method, 0.4659 gram of bismuth in 25 minutes. Taking it all in all, this is as good a method as we have for the determination of bismuth.

Summary.

(1) The apparatus is as simple as any electrolytic apparatus made.

(2) The deposition by this method is nearly as rapid as by the rotating anode and mercury cathode.

(3) The results are as accurate as those obtained by other methods where mercury is used as the cathode.

UNIVERSITY OF ARIZONA, TUCSON.

THE ESTIMATION OF SMALL QUANTITIES OF NITROGEN BY PELOUZE'S REACTION.

BY A. T. DAVENPORT.

Received July 2, 1910.

During some recent work, in which the writer was engaged, it became necessary to estimate very small quantities of nitrogen occurring in the form of nitrates. Various methods for the determination were tried, but none of those which are ordinarily satisfactory, quite supplied the needs in this particular case. Among all the methods tried, that which most nearly fulfilled all the conditions imposed was one in which the following reaction, originally employed by Pelouze, was used:

$$6FeCl_2 + 2KNO_3 + 8HCl = 3Fe_2Cl_6 + 2KCl + 4H_2O + 2NO.$$

More than fifteen different forms of apparatus, employing as many different methods of procedure, have been designed for the analysis of nitrates by the ferrous chloride reduction method. This variety in methods for conducting the analysis is evidence that it is difficult to get a process universally satisfactory, and also evidence that the determination is based on good fundamental principles, and worthy of effort spent to perfect the mechanical operation.

The development of methods has followed two distinct lines. In one direction, speed and ease of manipulation have been sacrificed for accuracy—this trend is illustrated in the extreme by Schlösing's intricate but accurate method of analysis. In the other direction, accuracy has been more or less neglected in an effort to eliminate all awkward operations and time-killing refinements, and here a method devised by P. Wagner easily leads the rest in so far as simplicity is concerned. Wagner collects the evolved nitric oxide over water in graduated cylinders, which are directly compared with a similar cylinder containing nitric oxide from a weighed amount of pure potassium nitrate, and kept, as nearly as possible, under the same conditions. The most generally used of the more refined methods in which high accuracy is maintained is that one worked out by Schultze, and modified by Tiemann. In Schultze-Tiemann's apparatus the liberated nitric oxide is collected in a jacketed burette over caustic soda solution, and the volume corrected to standard conditions according to the regular procedure in gas analysis. In the method to be described below, an effort has been made to combine the good points in Wagner's, and the Schultze-Tiemann methods, and to eliminate as many as possible of the defects.

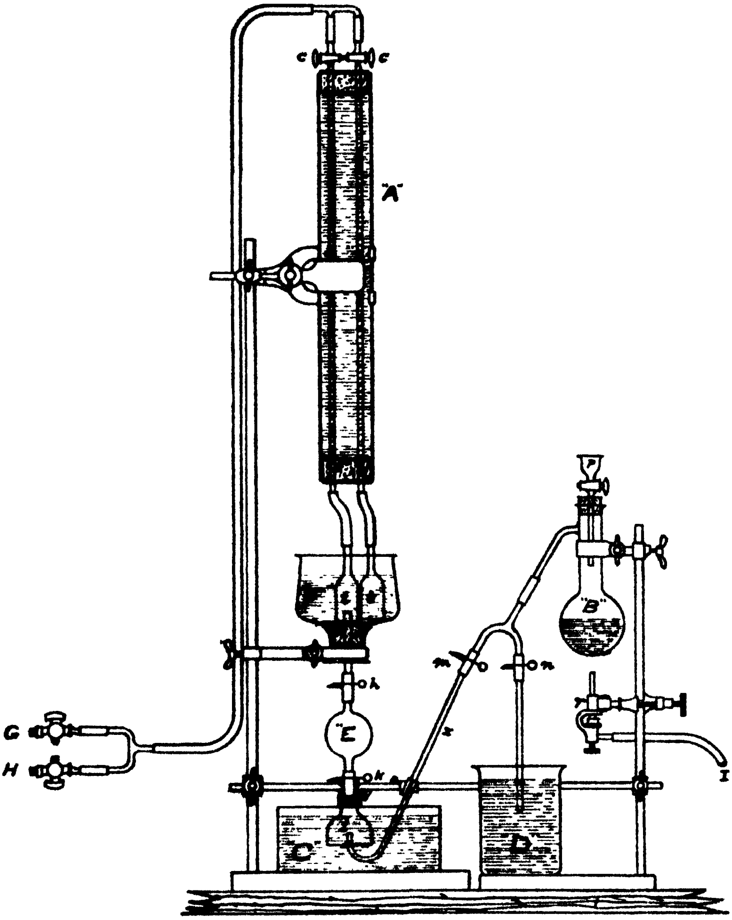
Some of the most important features found in the new method are: measurement of the gas volume over caustic soda solution in a jacketed burette graduated to 1/20 cc., as in the Schultze-Tiemann method, thereby insuring a thorough washing of the gas, and protecting it against sudden and local heating, or cooling, as may occur in Wagner's method. Correction of the gas volume by comparison with a standard volume contained in another burette under identical physical conditions which does away with lengthy calculations employed in the method of Schultze and Tiemann. Besides these features, the apparatus is so designed that it does away with several of the awkward operations belonging to the Schultze-Tiemann method, and thereby, approaches the simplicity of Wagner's procedure.

A description of the apparatus and method of operation is given below.

Details of Operation.

C and *F* are nearly filled with 25–27 per cent. caustic soda solution. By alternately opening pinchcocks *h* and *k* the caustic in *F* is allowed to replace the air in *E* and *l*. The stopcocks *cc* are opened and with a slight vacuum, the burettes are filled with caustic solution from *F*.

Next, 50 cc. of a nitrate solution, of a strength suitable to the capacity



A—Water jacket containing two burettes graduated to 1/20 cc.
B—Distilling flask in which the nitrates are decomposed.
C—Glass dish containing caustic soda solution.
D—Beaker of water to act as a seal.
E—Glass bulb filled with caustic soda for washing and cooling the nitric oxide.
F—Glass basin containing caustic soda from which the burettes are filled.
G—Compressed air
H—Vacuum.
I—Gas.
t, *t* and *l*—Glass bells for collecting gas.
p—A dropping funnel having a capillary stem.

of the burettes, is placed in the flask *B*. The pinchcock *n* is opened, and the gas burner, which is on a movable support *r*, is swung under the flask. When the liquid begins to boil, the flame is swung from under the flask, and *n* closed while *m* is opened to allow caustic from *C* to rise by suction in the outlet tube *x*, as far as the fork. Then *m* is closed, and the heating of *B* continued. As soon as pressure begins to develop in the flask, as shown by the inflation of the rubber connections, *n* is opened and all the air in *B* boiled out through the water in *D*.

Next, the flame is removed from under the flask, and *n* closed. As soon as a vacuum begins to form, 15 cc. each of concentrated ferrous chloride solution, and concentrated hydrochloric acid are introduced through the dropping funnel *p*, care being taken to close the stopcock before any air can rush through. The heating of *B* is renewed, and as soon as a slight pressure forms, the pinchcocks *m* and *k* are opened, when the liberated nitric oxide passes over and collects in *E*, where it is cooled and washed. After all the gas has passed over as shown by a cessation of bubbles, a partial vacuum is again formed in the flask, and the small amount of gas dissolved in the excess of ferrous chloride is extracted by the suction—upon reheating this residue of gas is driven over into *E*.

Next, one of the glass bells *t* is placed over the outlet from *E*, and pinchcock *k* closed, and *h* opened, when the gas passes up into the burette.

After standing for three minutes, the volume of the gas is noted. A standard nitrate solution is made by dissolving 1 gram of pure potassium nitrate in 250 cc. of distilled water. Under the conditions of the test one cc. of the standard solution gives practically 1 cc. of gas, so in case we have 10 cc. of gas in the above operation, 10 cc. of the standard solution are decomposed according to the above procedure, and the gas passed into the other burette for direct comparison with the neighboring gas volume.

At the completion of an analysis the stopcock *c* is opened, and compressed air carefully bubbled through *F*, when the burette is quickly swept free from nitric oxide.

A determination can be made in ten minutes, and the results of consecutive analyses agree very well as can be seen from the following table:

Analysis showed—

10 cc of solution to be equivalent to

10.55 cc. of NO, or	8.81 cc. of NO at 0° and 760 mm
10.60	8.85
10.60	8.85
10.50	8.77
10.65	8.89
10.60	8.85
10.70	8.93
10.65	8.89
10.61 Average	**8.86 Average**

Solutions of pure potassium nitrate were used, 1 gram of potassium nitrate in 250 cc. of water at 20°. Ten cubic centimeters of this solution are equivalent to 8.86 cc. of nitric oxide at 0° and 760 mm.

Considering the average volume 10.61 cc. of NO as being equivalent to 8.86 cc. of NO at 0° and 760 mm. the factor 0.835 was deduced with which the column of corrected volumes was obtained.

If there is a doubt as to whether the nitrate used for standard is pure, or whether all the gas is being driven over it is a simple matter to transfer the gas to a Hempel burette, and measure it under atmospheric pressure.

The direct comparison of gas volumes not only simplifies calculations, but also introduces the safeguards of a duplicate test against error.

The method of analysis has been in use at this laboratory for more than a year, and the article is published with permission of the E. I. du Pont de Nemours Powder Co.

EXPERIMENTAL STATION,
E I DU PONT DE NEMOURS POWDER CO.,
WILMINGTON, DELAWARE

THE ANALYSIS OF TIN-ANTIMONY ALLOYS.

BY LEROY W MCCAY.

Received August 9, 1910

The fact that hydrogen sulphide precipitates the antimony only from a dilute hydrofluoric acid solution containing tin in the higher and antimony in the lower stage of oxidation serves as an excellent means for the quantitative separation of these two elements.[1] If the solution be a hydrochloric or sulphuric acid one, the addition of hydrofluoric acid converts the metals into their fluorides, and the solution can then be diluted indefinitely without becoming turbid. The mixture of stannic sulphide, antimonious and antimonic sulphides and free sulphur obtained in the regular course of analysis was, until recently,[2] always dissolved in warm concentrated hydrochloric acid in a small platinum dish, hydrofluoric acid added, the solution filtered into a large platinum dish holding about 500 cc., and from the diluted solution the antimony precipitated in the cold with hydrogen sulphide as antimonious sulphide. The objection, however, to this method of dissolving the tin and antimony sulphides is that the accompanying sulphur, along with that which separates from the pentasulphide, forms, or seems to form, a protecting coating about some of the antimonious sulphide, so that it remains unattacked by the hydrochloric acid. Even after two extractions with the warm, concentrated acid antimony can generally be detected in the sulphur.

---

[1] THIS JOURNAL, 31, 373 (1909).

[2] The neutralization of the solution with sodium hydroxide and the addition to it, after introducing the hydrofluoric acid, of an excess of sodium acetate has proved unnecessary. See original paper, *loc. cit.*

If the treatment of the sulphides with the acid be carried out in a small flask attached to a reflux condenser, the reaction is soon complete, for here the acid can be boiled and kept boiling without there being any danger of antimonious chloride escaping. However, such a method for bringing the antimony into solution is far too tedious. The difficulty is avoided if concentrated sulphuric acid heated to strong fuming be employed as the solvent. The reaction goes on smoothly and rapidly, and is complete in from twenty to thirty minutes. The tin is converted into stannic, the antimony into antimonious sulphate. During the reaction, sulphur dioxide escapes along with the fumes of sulphur trioxide, and considerable sulphur volatilizes, a part of which condenses upon the clock-glass covering the dish in which the solution is made. The sulphur which remains is in the form of yellow or brown globules. I have tested it again and again for antimony, but have never found that it contained more than a trace. In each case the washed globules were dried and rubbed to a fine powder in an agate mortar, the mass was extracted with warm, concentrated hydrochloric acid, the solution filtered and hydrogen sulphide passed into the filtrate. Some attempts made to determine the antimony colorimetrically go to show that it never amounts to a tenth of a milligram. When the solution of the sulphates as above obtained is cool, it, together with the sulphur, is transferred to a small platinum dish with a minimum amount of water, the hydrofluoric acid added, the liquid heated, cooled, diluted and filtered (paraffined funnel) into the large platinum dish where the precipitation of the antimony with hydrogen sulphide is made. A platinum or paraffined glass tube is used for introducing the gas into the solution. The antimonious sulphide precipitated from a sulphuric acid solution containing hydrofluoric acid is pure, barring a trace of sulphur which can be rapidly and completely extracted with a mixture of equal parts of absolute alcohol and carbon disulphide.[1] Dried at 110° it is free from water, nor does it after such drying suffer any loss when heated to blackness in a current of carbon dioxide. The sulphide is not absolutely insoluble in the liquid from which it is thrown down. The solubility, however, is very small, and can in most cases be neglected. Some experiments made with Kahlbaum's purest antimony indicate that the filtrates from the sulphide contain on an average 0.0004 gram antimony.[2] The solubility seems to increase with the quantity of hydrofluoric acid employed. When just enough of the latter (8–10 drops of a 48 per cent. solution) is added to prevent hydrolysis, the precipitation of the antimony by hydrogen sulphide is complete.[1] The sulphide is best collected in a Neubauer crucible and washed with water saturated with hydrogen sulphide and strongly acidified with acetic acid. The filtrate is evaporated in platinum on the sand bath, heated to fuming, and the thick liquid poured into a liter of water:

---

[1] Thiele, *Z anal Chem.*, 30, 479

[2] The volume of the solution from which the antimony was in each case precipitated amounted to roughly 450 cc. The solution contained 8–10 cc. concentrated sulphuric acid and 5 cc. hydrofluoric acid.

$$Sn(SO_4)_2 + 4H_2O = H_4SnO_4 + 2H_2SO_4.$$

Before weighing, the stannic oxide should be strongly ignited in the presence of ammonium carbonate.

Concentrated sulphuric acid heated to fuming or, if necessary, to boiling is also admirably adapted for decomposing the alloys of tin and antimony. Unless the amount of lead in such an alloy be very great it remains behind as pure lead sulphate which, after diluting the solution somewhat, adding hydrofluoric acid and then water and alcohol, can be filtered off, washed, dried and weighed. The advantage of separating and determining the lead at this stage of the analysis, and in such a simple manner, will be evident to all familiar with the difficulties ordinarily encountered in separating lead from antimony. The filtrate is caught in a paraffined beaker, one of ceresin,[2] or in the large platinum dish placed under a bell-jar resting on a ground-glass plate, and furnished with the necessary adjustments for filtering by suction. The hot sulphuric acid converts the tin into stannic, the antimony into antimonious sulphate. The alloy should be in the form of filings or very fine borings, and the treatment with the acid carried out in a covered porcelain or quartz dish, heated on the sand bath. Half an hour after the acid commences to fume strongly the decomposition is ordinarily complete, and the contents of the dish are then transferred to one of platinum in which 5 cc. of hydrofluoric acid[3] diluted with 20 cc. of water have been placed. The stannic and antimonious sulphates are converted into fluorides, while the lead sulphate remains undissolved. When hard leads and type metal containing over 50 per cent. of lead are treated in this way the resulting lead sulphate is apt to be gray and contain several milligrams of antimony. In such a case the lead sulphate should, after drying, be mixed with six times its weight of a mixture of equal parts of sulphur and sodium carbonate, and fused in a covered porcelain crucible at a barely red heat for fifteen minutes. In making this fusion I find it best to use a small burner flame about 5 cm. long. The ring carrying the triangle and crucible is lowered until the tip of the flame not only touches

[1] This observation and the fact that the antimonious sulphide when dry is free from all foreign matter have led me to undertake a revision of the determination of the equivalent of antimony.

[2] Baker Chem. Co , Phillipsburg, N. J.

[3] The amount of hydrofluoric acid necessary will depend, of course, on the quantities of tin and antimony present. For all of the alloys which I have thus far examined 5 cc. of the 48 per cent. acid have proved sufficient.

the bottom of the crucible but spreads out so as to lick the sides to some extent. The mixture of sulphur and antimony sulphides obtained by acidifying the sulpho-salt solution is dried, dissolved in a small amount of hot, concentrated sulphuric acid, diluted somewhat, a little hydrofluoric acid added (small platinum dish), and the filtrate from the sulphur combined with the main tin and antimony solution. The lead sulphide is then converted into the sulphate and weighed as such.

Hydrogen sulphide precipitates from the filtrate from the lead sulphate not only the antimony but any copper which may be present.[1] Their separation is best effected with colorless sodium sulphide or hydrosulphide. Mr. G. W. Thompson uses for this purpose a concentrated solution of potassium hydroxide. Although I prefer the colorless sodium sulphide as a solvent for the antimonious sulphide, the method of Mr. Thompson has given me very satisfactory results. The cupric sulphide can be dissolved in nitric acid and the copper determined electrolytically. To determine the antimony I collect the precipitate from the sulpho-salt solution in a Gooch crucible and heat it to blackness in a current of carbon dioxide. The operation is conducted as follows: The crucible with its contents is placed in a ring on the end of a platinum wire and lowered to the bottom of a large test tube of hard glass. The test tube which is 25 cm. long and 4.2 cm. internal diameter, is clamped at an angle of 45°, so that the lower end is about 35 cm. above the top of the table, and closed with a doubly perforated rubber stopper carrying two tubes. The one through which the carbon dioxide is introduced passes through the center of the stopper and is shoved down until the end is just opposite the mouth of the crucible; the lower end of the other tube, which is short, is flush with the stopper, and simply serves for the escape of the gas. When all the air in the test tube has been displaced by carbon dioxide, the upper part of the full flame of a Bunsen burner is moved briskly around and in contact with the bottom of the tube, and in from fifteen to twenty minutes all the sulphur is driven off. During the operation, I have never noticed the volatilization of any antimonious sulphide due to overheating. The apparatus is exceedingly simple, and the results obtained with it leave little to be desired. The crucible should cool in the current of carbon dioxide. To remove the crucible without having it come in contact with the condensed sulphur, slip a piece of glazed paper down the tube and draw the crucible up over it.[2]

The filtrate from the antimonious and cupric sulphides is heated in a platinum dish on the sand bath, and when the water and most of the hydrofluoric acid have evaporated, the remaining liquid is heated more strongly until sulphuric anhydride fumes are given off freely. When the solution has cooled it is poured at once into an excess of water. The hydrolysis of the stannic sulphate can be hastened by neutralizing most of the free acid with ammonia water and heating the solution to boiling. Equally good results can be obtained by precipitating the tin as stannic sulphide and converting this into the oxide by roasting, or by transforming the sulphate into the double oxalate of tin and ammonium and determining the metal electrolytically according to Classen's method.

---

[1] Bismuth, cadmium and arsenic(ous) are also precipitated. Since the alloys thus far examined by me contain no bismuth or cadmium, and only traces of arsenic, the separation and determination of these elements have not been considered.

[2] Henz, *Z. anorg. Chem.*, 37, 11 (1903).

Since I have received a number of letters requesting information as to the details of the general scheme observed by me in applying this hydrofluoric method to the analysis of tin-antimony alloys, I would say that the following course of procedure will be found satisfactory in most cases. If the directions given are in places not sufficiently full and clear, the reader is referred to the preceding pages.

Place from 0.5–1.0 gram of the alloy, preferably in the form of filings or fine borings, in a quartz or porcelain dish, cover the dish with a clock-glass, and introduce through the lip 10 cc. of concentrated sulphuric acid. Place the dish on the sand bath, heat it rapidly until fumes of sulphuric anhydride begin to escape, and continue the heating for about half an hour. If at the end of this time the solution is clear, and the underlying lead sulphate pure white, remove the dish from the bath, let it cool, and transfer its contents at once to a platinum dish of 250 cc. capacity containing 5 cc. 48 per cent. hydrofluoric acid and 20 cc. of water. Use a rubber-tipped rod and the least possible amount of water for removing the lead sulphate adhering to the porcelain dish. Heat the solution to boiling, stirring all the time with a platinum spatula to prevent bumping. Dilute to 150 cc., cool, add 50 cc. of 95 per cent. alcohol, stir, and let the lead sulphate settle. Collect the lead sulphate in a Neubauer crucible, or on a filter paper fitted in a paraffined funnel, wash thoroughly with water containing one-fourth its volume of alcohol and a little sulphuric acid, dry, ignite, and weigh. If the Neubauer crucible is used, place it in a larger one of porcelain and then ignite. When the alloy contains more than 50 per cent. of lead the sulphate is apt to be gray and contain antimony. In such a case the sulphate should be fused with soda and sulphur according to the directions already given. The filtrate from the lead sulphate, as above obtained, is caught in the large platinum dish placed under the bell-jar provided with the various adjustments for filtering by suction. To avoid splashing it will be found well to cover the dish with a paraffined clock-glass with a hole in the center, through which the end of the stem of the funnel or crucible support is passed. Dilute the filtrate to about 450 cc. and introduce the hydrogen sulphide through a platinum or paraffined tube which is suspended above the center of the dish and lowered until the end in the solution is a centimeter above the bottom of the dish. Let a rapid current of the gas pass through the solution for one hour. Permit the precipitate to subside, filter and wash with water containing acetic acid and saturated with hydrogen sulphide. Suck the precipitate as dry as possible, unfold the filter paper and spread it out in a shallow porcelain dish, add some colorless moderately concentrated sodium sulphide, cover with a clock-glass, and place on the water bath. Add water, filter off the clear fluid, treat the residue again with sodium sulphide, digest a short time, repeat the same operation a third time, bring the residue onto the filter, and wash it with water containing a little sodium sulphide. Dissolve the cupric sulphide in nitric acid and determine the copper electrolytically. Collect the precipitate obtained by acidifying the sulpho-salt solution with sulphuric acid in a Gooch crucible, wash it with water containing hydrogen sulphide, dry and heat it to blackness in a current of carbon dioxide in the apparatus described. The tin in the filtrate from the cupric and antimonious sulphides can be determined according to any one of the three methods mentioned above.

Personally, I prefer to throw down the tin in the form of stannic acid by pouring the thick sulphuric acid solution into an excess of water. The stannic acid so obtained is very pure, barring a little sulphuric acid which, however, is readily expelled by igniting the stannic oxide in the presence of ammonium carbonate.

Mr. G. W. Thompson, of the National Lead Co., has very kindly sent me two alloys which I have analyzed according to the above scheme. Mr. Thompson has also given me the formulas according to which the alloys were prepared, and furnished me the analyses. His process for separating tin from antimony is a modification of the Clarke method.[1] Alloy 2 was also examined by one of our fellows, Mr. H. E. Rankin, who analyzed it according to both the Thompson and hydrofluoric acid methods.

Alloy 1.—Samples taken at random from various parts of the bottle did not give me sufficiently constant results, so I took from the bottom of the mass about five grams which, since the alloy is quite brittle, I ground to a fine powder in an agate mortar. This powder was employed in making the analyses. My results, along with those reported, are given in the following table.

I did not examine the alloy for arsenic. In each case the amount of lead sulphate obtained was too small to weigh. This alloy does not seem to be homogeneous in composition.

---

[1] Private communication. See also his paper, "Method of Analysis of Alloys of Lead, Tin, Antimony and Copper," *J. Soc. Chem. Ind.*, 15, 179 (1896).

Constituents.	Formula Per cent.	Reported.	HF-method.	HF-method.
Lead....	..	0.26	trace	trace
Antimony	40	39.32	38.35	38.30
Tin...	60	60.42	61.38	61.47
Copper..		0.13	0.14	0.13
Arsenic		trace	. .	....
	100	100.13	99.87	99.90

Alloy 2.—The results of both methods agree in a very gratifying way, as will be evident from an inspection of the following table:

Constituents.	Formula. Per cent	Reported. Per cent	Rankin. Thompson-M.	Rankin. HF-M	McCay. HF-M.
Lead	48	47.38	47.41	47.34	47.43
Antimony	10	10.42	10.45	10.43	10.33
Tin	40	40.30	40.44	40.44	40.42
Copper . . .	2	1.88	1.89	1.73	1.80
Arsenic . .		0.06	..	...	.
	100	100.04	100.19	99.94	99.98

No attempts were made to determine the arsenic. The alloy is undoubtedly very homogeneous in composition.

The fact that this method for separating tin from antimony involves the use of a platinum dish holding 500 cc. militates seriously against its general use.[1] I have recently found that the analysis of an alloy can be made in glass vessels, provided one possesses a platinum dish holding 250 cc. in which the lead sulphate can be separated from the tin and antimony with the rather concentrated hydrofluoric acid, and the filtrate from the cupric and antimonious sulphides evaporated to fuming in order to expel the acid. The hydrofluoric acid solutions are so dilute during the other operations that they have little action on good glass, and the salts formed all remain in solution provided one works rapidly. The solution left on evaporating in platinum the filtrate from the cupric and antimonious sulphides contains a little calcium sulphate and possibly some silica; but on diluting the solution the former dissolves and the latter can, if necessary, be filtered off. Of course, the dilution should not be too great, nor should the diluted liquid be heated prior to filtration, for hydrolysis might take place and some stannic acid separate out. I have analyzed both alloys, using an ordinary 250 cc. platinum dish, and Jena beakers, with the following results:

Now these results are fully as good as those obtained by working entirely in platinum. In closing I would say that by first treating alloys very high in lead with dilute nitric acid, evaporating, and then adding concentrated sulphuric acid and heating to fuming, the alloys appear to be completely decomposed. Whether in the presence of such large amounts of lead sulphate 5 cc. of 48 per cent. hydrofluoric acid are sufficient to transform all the accompanying stannic and antimonious sulphates into fluorides remains to be seen. Any antimonic acid formed by the nitric acid can be reduced to antimonious oxide by sprinkling some sulphur over the concentrated sulphuric acid, after all the nitric acid has been expelled, and again heating to strong fuming for about fifteen minutes. The reduction is of course effected by the sulphur dioxide formed.

---

[1] O. Brunck, Private communication. Th. Döring, *Chem. Ztg.*, **34**, 747.

	1. Per cent.	2. Per cent.
Lead	trace	47.41
Antimony	38.30	10.46
Tin	61.30	40.40
Copper	0.12	1.82
Arsenic	....	....
	99.72	100 09

PRINCETON., N. J.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY]

THE DETERMINATION OF INDIUM WITH THE USE OF A MERCURY CATHODE.

BY LILY G. KOLLOCK AND EDGAR F. SMITH.

Received July 23, 1910.

Thiel[1] recommends the use of a silver-plated platinum cathode for the deposition of metallic indium. Dennis and Greer[2] found that this metal may be readily precipitated on a rotating platinum dish cathode from solutions of its chloride or nitrate in the presence of pyridine, hydroxylamine or formic acid.

The purpose of the present communication is to offer the results obtained in the electro-analytical behavior of indium toward a mercury cathode.

A solution of indium sulphate (10.15 grams of metal in 500 cc.) containing a small amount of free acid was the electrolyte. A mercury cup of the usual form was employed.[3] The method followed and precautions taken were identical with those described in the determination of other metals with the same apparatus.

With a total dilution of 10 cc., a current varying from 2 to 4 amperes, an e. m. f. of 7.5 to 6.5 volts, and an anode rotating 750 times per minute, the following results were obtained:

0.1013, 0.1008, 0.1010, 0.1013, 0.1011, 0.1010, 0.1011, 0.1011 gram

---

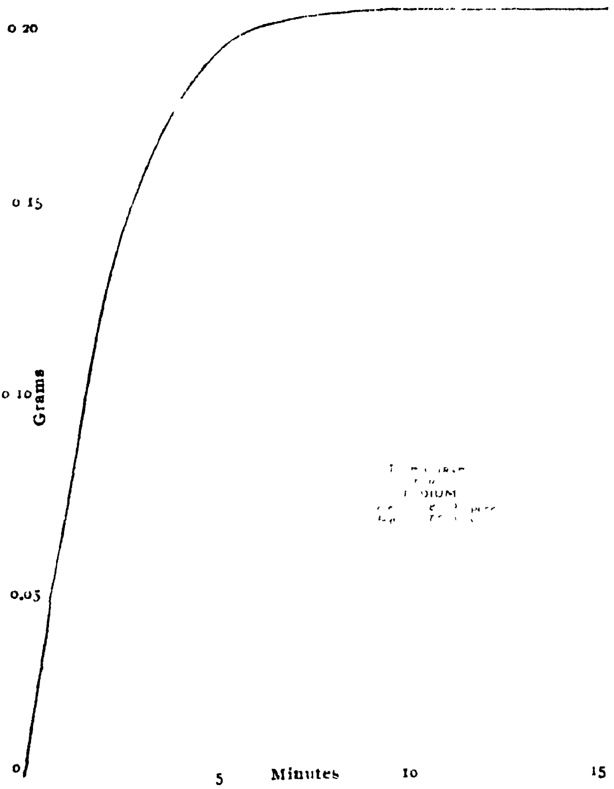
[1] *Z. anorg. Chem.*, 39, 119.

[2] *Ber.*, 37, 75; THIS JOURNAL, 26, 438.

[3] Smith's *Electro-analysis*, p. 58, 4th Ed.

The time for actual electrolysis was 15 minutes. Doubling the quantity of solution also gave concordant results after 18 minutes' action of the current:

0.2021, 0.2021, 0.2020, 0.2021, 0.2019, 0.2021 gram



The accompanying time curve was made under the following conditions:

Vol. of sol	10 cc.
Indium present	0.2020 gram
Current strength	2.5 amperes
E. m. f.	7.5–5.5 volts
R. p. m. of anode	750

Dr. John Frazer, of this Laboratory, conducted a number of determinations of indium, using a platinum cathode with a platinum spiral anode, rotating 250 to 400 times per minute. In the presence of 0.1 cc. of concentrated sulphuric acid and a few drops of gelatin a beautiful, adherent deposit of indium was obtained with a current of N. D_{100} = 3 amperes and a pressure of from 4.5 to 5 volts. The precipitation was complete in twenty-five minutes.

A potassium cyanide electrolyte proved satisfactory; while in the presence of 2 grams of sodium acetate, 0.2 cc. of normal acetic acid and several drops of gelatin, a current of 5.6 amperes and 4 volts deposited the metal in a beautiful, adherent form in forty minutes. The temperature of the electrolyte was maintained at 60°. The most satisfactory deposits of this metal were obtained, however, from an electrolyte containing from 0.75 gram to 1.5 grams of Rochelle salt. They were brilliant in appearance and perfectly adherent. They resembled such coatings as are produced by fresh aluminium paint. They were preserved without alteration or loss of luster.

UNIVERSITY OF PENNSYLVANIA

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 180.]

A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF MANGANESE.

BY F J METZGER AND ROBERT F MCCRACKAN

Received July 20, 1910

In a previous number of THIS JOURNAL[1] mention was made of the fact that manganese, in sulphuric acid solution, was oxidized to the quadrivalent form by means of sodium bismuthate, and that the manganese remained in solution in this state of oxidation. It is the purpose of this paper to describe a method based on the above principle whereby the manganese may be accurately determined.

Solutions Used.—A 0.1 *N* potassium permanganate solution, and a solution of ferrous sulphate of about equivalent strength. A solution of manganous sulphate was prepared and carefully standardized gravimetrically by weighing as pyrophosphate.

Method.—Place 50 cc. of the standard manganese solution in a 300 cc. Erlenmeyer flask, add 10–15 cc. of concentrated sulphuric acid and allow to cool. Add 1–2 grams of finely powdered sodium bismuthate in such a way that none of the powder sticks to the sides of the flask. Place the flask in a beaker of water so that the level of the solution is several inches below the level of the water in the beaker. Heat slowly to boiling and boil till the precipitate of basic bismuth compound settles well and has a granular appearance (about 20 minutes' boiling is usually necessary). Remove the flask and cool under running water, add a known excess of ferrous sulphate solution, dilute to about 200 cc. and titrate back with standard permanganate solution.

---

[1] Metzger and Heidelberger, THIS JOURNAL, 32, 643.

The manganese standard of the permanganate is calculated from the reaction which may be represented thus:

$$Mn^{++++} + 2Fe^{++} \longrightarrow Mn^{++} + 2Fe^{+++}.$$

Or the value of the permanganate in terms of iron multiplied by 0.4918 gives the value in terms of manganese.

The following table of results will give an idea of the accuracy of the method:

No.	Mn taken.	Mn. found	Error.
1	0.0981	0.0979	−0.0002
2	0.0981	0.0975	−0.0006
3	0.0981	0.0973	−0.0008
4	0.0981	0.0974	−0.0007
5	0.0981	0.0980	0.0001
6	0.0981	0.0981	±0.0000

The method is quite rapid and the end point is sharp and distinct, being the usual pink color in a solution containing a white precipitate. The application of the method to the analysis of spiegel and manganese ores is now under way, and we hope to work out a method which will be rapid and accurate and not possess the disadvantages inherent in the Volhard method.

QUANTITATIVE LABORATORY

THE USE OF ORGANIC ELECTROLYTES IN CADMIUM SEPARATION.

BY MARY E HOLMES AND MARY V DOVER

Received August 1, 1910.

In a previous paper[1] it was shown that currents below one ampere possess undoubted advantages for electrolytic separations when the rotating anode is employed, that study was concerned with the separation of cadmium from the metals of Groups III and IV and from magnesium at currents of 0.3-0.4 ampere, using the sulphuric acid and also the acetate electrolyte, and comparing the results obtained with those of other investigators working at high currents. It was clear that the possibilities of work in the line of electrolytic separations were almost limitless and that the work on cadmium alone called for a much more extended investigation, using other metals and a greater variety of electrolytes.

The present work was undertaken in order to test further the usefulness of low currents in cadmium separations. The alkaline earth metals were used and the acetate, formate, and lactate electrolytes. Corresponding separations were made with both low and high currents (*i. e.*, five amperes), but in no case did the high currents prove desirable. Whether cadmium was used alone or in presence of other metals, the deposits were dark in color, spongy, not adherent, difficult to dry, and in most cases very evidently not worth weighing. Whenever they were weighed, the results were very high. In the case of low currents, however, interesting and accurate results were obtained, though the deposits varied considerably in character and in accuracy with the different electrolytes employed.

---

[1] THIS JOURNAL, 30, 1865.

During this work it has been evident that each variety of ion present in the solution exerts a very definite influence on the deposit. The presence of two kinds of ions in a solution may produce a decidedly different deposit from that obtained by the influence of either ion alone. For instance, in the previous work conducted with cadmium sulphate solutions with the sulphuric acid electrolyte, smooth adherent deposits of fine crystalline structure were obtained. The deposits from a cadmium sulphate solution using the acetate electrolyte were more coarsely crystalline, and if another metal were present, *e. g.*, aluminium, the crystals tended to sponginess and therefore to occlusion of the mother liquor, unless carefully washed with hot water. These same conditions were observed when a cadmium acetate solution was used with the acetate electrolyte, so that in general it may be said that the sulphate ion aids in forming a finely crystalline, compact deposit, while the acetate ion causes the deposit to be more coarsely crystalline with a tendency to sponginess. The presence of the sulphate ion always seems to improve the character of a deposit, no matter what other ion may be present.

As in the previous work, a platinum dish of about 200 cc. capacity was employed as the cathode, but as a dish anode was not available, the ordinary spiral anode was used, the time required being not much more than is necessary with the dish anode, *i. e.*, forty-five minutes to one hour. It is possible that the dish anode may produce firmer deposits, but certainly the spiral anode has proved to be very useful in such cases. Solutions of cadmium salts containing not more than 0.2 gram of cadmium metal in 10 cc. were used.

I. The Acetate Electrolyte.[1]

The acetate electrolyte was first suggested since it was impossible to use the sulphuric acid electrolyte with all the alkaline earth metals. To 10 cc. of cadmium acetate solution, 2 grams of ammonium acetate and 1 cc. of acetic acid were added, the solution diluted to about 125 cc., heated to the boiling point, and electrolyzed for one hour, using 0.3 ampere and 2.4–3 volts. As a result, 0.1744 gram of cadmium was repeatedly deposited and the remaining solution showed no test for cadmium when treated with hydrogen sulphide. Then a series of separations was made of cadmium from the alkaline earth metals under the same conditions. About 0.2 gram of metal was represented by the amounts of calcium, strontium, and barium acetate solutions used. Two separations from calcium gave 0.1744 gram of cadmium, two from strontium, 0.1742 gram and 0.1744 gram respectively, and one from barium 0.1746 gram. Another separation was tried from a mixture of all three metals, calcium, strontium, and barium, the cadmium obtained weighing, as before, 0.1746 gram.

---

[1] This Journal, 27, 1275.

Owing to the fact that calcium sulphate is comparatively easily soluble, it was found that the separation of cadmium from calcium is possible, using a cadmium sulphate solution with an acetate electrolyte. Better results were obtained, however, when the free acid was omitted from the electrolyte. To 10 cc. of a cadmium sulphate solution, 2 grams of ammonium acetate were added, the solution diluted as usual, and after heating to the boiling point, electrolyzed, using 0.3 ampere and 2.5–3 volts for one hour. In two successive determinations, 0.1968 gram and 0.1970 gram were deposited, no test for cadmium being obtained in the solution. When 1 gram of calcium acetate was added to 10 cc. of the same cadmium sulphate solution and electrolyzed under the same conditions, 0.1968 gram of cadmium was obtained. These deposits were very satisfactory, clean and smooth, with few crystals of any size, easily washed and dried, showing the valuable influence of the presence of the sulphate ion. The character of the deposit was not changed by the presence of calcium. Determinations corresponding to these were made, using as electrolyte 1 cc. of acetic acid in addition to the 2 grams of ammonium acetate. The character of the deposits was almost as good as in the other cases, but the weights were low. From the cadmium sulphate solution alone, only 0.1958 gram and 0.1956 gram were deposited in two successive trials instead of 0.1968 gram. In presence of 1 gram of calcium acetate, 0.1960 gram and 0.1962 gram were obtained. The solutions all gave slight tests for cadmium with hydrogen sulphide. Hence it was concluded that in these cases the free acid hindered the complete precipitation of the cadmium. Similar trials were made, using the cadmium sulphate solution with strontium and barium acetates, but as was to be expected, precipitates of strontium and barium sulphates interfered with the work.

II. The Formate Electrolyte.[1]

The effect of the formate electrolyte was next investigated Conditions were first determined for the complete deposition of cadmium from a cadmium formate solution; then the separation of cadmium from calcium, strontium, and barium was effected, using the formates of these metals. The electrolyte used was ammonium formate in presence of formic acid. With 10 cc. of the cadmium formate solution were mixed 2 grams of ammonium formate and 1 cc. of formic acid, the solution diluted as usual, heated to the boiling point, and electrolyzed for forty-five minutes, using 0.3 ampere and 1–2 volts. In one trial, 0.1942 gram of cadmium was deposited and again, 0.1944 gram. In presence of 1 gram of calcium formate, under the same conditions, 0.1944 gram of cadmium was obtained. Using 1 gram strontium formate, the deposit weighed 0.1946 gram, and with 1 gram barium formate, 0.1946 gram. In all these cases, no other ion was present except the formate ion, so that the character of the deposits was due entirely to that ion. Whereas the deposits were crystalline and adherent and of good color, and the weights obtained were concordant, very careful washing was necessary, particularly when the alkaline earth metals were present. The results on the whole were better than when the acetate electrolyte was used alone.

---

[1] THIS JOURNAL, 27, 1275.

When cadmium sulphate solution was used, however, with the formate electrolyte, very excellent deposits were obtained, showing again the influence of the sulphate ion. To 10 cc. of the same cadmium sulphate solution (containing 0.1968 gram of cadmium metal in 10 cc.) were added 2 grams of ammonium formate and 0.5 cc. of formic acid. After diluting and heating to the boiling point, the solution was electrolyzed for one hour, using 0.3 ampere and 0.8–1 volt. A deposit was obtained weighing 0.1968 gram. In another trial 0.1970 gram of cadmium was obtained. Upon the addition of 1 gram of calcium formate, using similar conditions, 0.1968 gram of cadmium again came down. The deposit seemed not to be altered in any way by the presence of calcium. Some free acid was found necessary in all these determinations, as cadmium formate is somewhat difficultly soluble; and if a formate is used alone as electrolyte, a white precipitate of cadmium formate interferes with the work.

A third series was made using cadmium acetate as a starting point with the formate electrolyte. From 10 cc. of a cadmium acetate solution, it was found that the cadmium could be fully deposited in forty-five minutes, using 0.3 ampere and 0.8–1 volt, the electrolyte being as before 2 grams of ammonium formate and 0.5 cc. of formic acid. The deposit weighed 0.1760 gram. Mixed with 1 gram of calcium formate, 0.1760 gram of cadmium was obtained; and with 1 gram of strontium formate and 1 gram of barium formate, respectively, 0.1762 gram and 0.1760 gram of cadmium were thrown down. The character of these deposits was also good, though perhaps not quite so firm as in the case of those obtained from the sulphate with the formate electrolyte. The deposits were finely crystalline and adherent, but slightly porous.

III. The Lactate Electrolyte.[1]

The action of the lactate electrolyte was then investigated. As before, the first trial was made with only lactate ions present. The electrolyte used was 2 cc. of lactic acid with 1 cc. of ammonium hydroxide. This was added to 10 cc. of a solution of cadmium lactate, diluted as usual, and electrolyzed at boiling temperature for one hour, using 0.3 ampere and 2.8–3 volts. The weights of cadmium obtained, although fairly concordant, were not considered reliable. The greater part of the deposit was fine and adherent, but had also coarse crystalline plates which scaled off and were not easily handled. Again, however, the use of the same electrolyte with the cadmium sulphate solution resulted in the formation of a very excellent deposit. It was silvery-white, very finely crystalline, clean, and easy to wash. The same excellence was seen in the metal deposited from the cadmium sulphate solution in presence of 1 gram of calcium lactate. To 10 cc. of cadmium sulphate solution were added 2 cc. of lactic acid and 1 cc. of ammonium hydroxide, the solution diluted, heated to boiling, and electrolyzed for one hour with a current of 0.3 ampere and 2.6–3 volts. The weights of cadmium obtained in two trials were 0.1964 gram and 0.1966 gram. When 1 gram of calcium lactate was added, 0.1966 gram and 0.1965 gram were successively obtained.

---

[1] This Journal, 27, 1275.

An attempt was made to use cadmium acetate solution with the lactate electrolyte, but the deposits again showed coarse crystalline plates which scaled off in washing and the weights were always low.

With a solution of cadmium formate, however, the results were better. Although the same tendency to scaling off was observed, it could be controlled more easily. It was found better to make the quantity of lactic acid a little less, a scant 2 cc. giving the best results. From 10 cc. of the cadmium formate solution used, 0.1944 gram of cadmium had been previously obtained. Using the same amount of this solution, with 2 cc. of lactic acid and 1 cc. of ammonium hydroxide, diluting, and heating to the boiling point, 0.3 ampere and 2–3 volts used for one hour gave successively 0.1944 gram and 0.1946 gram of cadmium. A series of separations was then tried from calcium, strontium, and barium. On adding 1 gram of calcium formate to the solution as prepared above, 0.1946 gram of cadmium was obtained; with 1 gram of strontium formate 0.1944 gram, and with 1 gram of barium formate 0.1946 gram of cadmium was precipitated. The character of the deposit was not materially altered by the presence of the alkaline earth metals, although with the barium formate, there seemed to be a tendency towards the formation of coarser crystals.

In conclusion, it seems evident that in work with the rotating anode:

1. Low currents are preferable for the deposition of cadmium, when organic electrolytes are used.

2. Each electrolyte has a decided influence on the character of the deposit, which is not to be foreseen.

3. A mixture of ions improves the character of the deposit. This is most evident when the sulphate ion is present, the best deposits being

obtained from the cadmium sulphate solution, using the acetate, formate, or lactate electrolyte. The formate ion also seems to exert a good influence on the deposit, cadmium acetate solution with the formate electrolyte giving satisfactory results even in presence of the alkaline earth metals, and cadmium formate solution with the lactate electrolyte also giving good deposits. It is of interest to observe that the acetate and lactate electrolytes when used alone are not so successful, and the combination is an extremely poor one.

It is clear that other organic electrolytes should be investigated, and that many interesting and valuable relations may be found in the comparison of the nature of the deposits from different electrolytes and from their combinations. It is hoped that this investigation may be continued in this laboratory.

MOUNT HOLYOKE COLLEGE,
SOUTH HADLEY, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

DETERMINATION OF AMMONIA NITROGEN IN WATER IN THE PRESENCE OF HYDROGEN SULPHIDE.

BY EDWARD BARTOW AND B. H. HARRISON.

Received July 4, 1910.

The tests for free and albuminoid ammonia, since their introduction in 1867, have played an important role in the sanitary examination of drinking-water. They have been criticized because of inaccuracies due to interferences from substances in solution, and it is this phase of the subject that we have been investigating. In the experimental work we have taken the usual precautions to have a uniform rate of distillation, a uniform temperature for Nesslerization, a uniform organic content in comparative tests, all glass apparatus and a room free from ammonia fumes. As an illustration of the necessity for the last precaution we found that 0.036 part per million of ammonia nitrogen was added to a water exposed for 24 hours in the distilling room, which adjoined a room where dogs were kept for experimental work in physiological chemistry, and that 0.566 part per million was added to water in the room where the dogs were kept.

Natural waters sometimes contain substances which may cause interference if these combine with ammonia to prevent its distillation or if they are distilled with the ammonia and interfere with the Nessler test. Of the former class are acids like sulphuric acid, which, as is well known, must be neutralized before distillation. Of the latter class is hydrogen sulphide, which will distil over with the ammonia and will give false results.

We have studied the effect of three substances, calcium acid carbonate, magnesium chloride and hydrogen sulphide. Our results indicate that calcium acid carbonate and magnesium chloride in the amounts ordinarily found in natural water do not interfere materially with the determination of free ammonia. Kober[1] has stated that in the presence of magnesium chloride all the ammonia is not given off. This may be true if the concentration of the magnesium chloride is very high. Our experiments with an amount of magnesium chloride in excess of the amounts found in any of the Illinois water supplies lead us to conclude that the interference is not material

Hydrogen sulphide, however, interferes with the Nessler test. When the amount of ammonia is large the hydrogen sulphide might be removed by precipitation with a lead or zinc salt and the ammonia determined by direct nesslerization, but if small and it is desirable to distil and nesslerize the distillates, the results are very inaccurate. This is shown in our first test. We added 0 06 part per million of ammonia nitrogen to a water in which 56 parts per million of purified hydrogen sulphide gas had been absorbed. Nesslerization after distillation showed 0 082, 0.214 and 0 376 part per million of nitrogen when only 0 06 part per million had been taken. A repetition of the experiment gave similar inaccurate results.

The hydrogen sulphide must evidently be prevented from interfering either by distilling it off in the presence of something that will hold the ammonia or in holding it back while the ammonia is being distilled. The use of sulphuric acid to retain the ammonia in the Kjeldahl process led us to try it To 500 cc. of a water containing 20 parts per million of hydrogen sulphide and a known amount of ammonia nitrogen, 50 cc. of normal sulphuric acid was added and 100 cc. of water distilled over. The first tube was cloudy and smelled strongly of hydrogen sulphide gas; the second tube was practically clear. 50 cc. of a normal solution of sodium hydroxide was then added and 200 cc. of water distilled and nesslerized. On the first series with 0 06 part per million taken 0 082,

TABLE I. DETERMINATION OF AMMONIA NITROGEN IN THE PRESENCE OF HYDROGEN SULPHIDE. RESULTS IN PARTS PER MILLION

Total N found.	Correction.	Nitrogen found.	Nitrogen taken.
0 082	0 026	0 056	0 060
0 086	0.026	0 060	0.060
0.082	0.026	0 056	0.060
0 416	0.030	0.386	0.400
0 400	0.030	0.370	0.400
0.136	0.020	0.116	0.120
0 256	0.020	0.236	0.240
0.528	0.020	0.508	0.500
1.040	0.020	1.020	1.000
2.000	0.020	1.980	2.000

---

[1] THIS JOURNAL, 30, 1279–81.

0.080, 0.078 and 0 082 part per million was found. This showed the necessity for control tests which were run in succeeding series. The readings with the corrections are shown in Table I. The results are sufficiently accurate.

With respect to the holding of the hydrogen sulphide and the distillation of the ammonia, the addition of sodium hydroxide would not be satisfactory as the sodium sulphide formed would hydrolyze and hydrogen sulphide would be found in the distillate.

Phelps,[1] in discussing the direct nesslerization of sewage, suggests the precipitation of the hydrogen sulphide with lead or zinc acetate. We have tried lead acetate and have compared it with the sulphuric acid method, as shown in Table II:

TABLE II. DETERMINATION OF AMMONIA NITROGEN BY ADDITION OF SULPHURIC ACID OR LEAD ACETATE. RESULTS IN PARTS PER MILLION

Total N found.	Correction.	Nitrogen found.	Nitrogen taken	Method.
0.090	0.029	0.061	0.060	Sulphuric acid
0.088	0 029	0.059	0.060	Sulphuric acid
0.094	0 034	0 060	0.060	Sulphuric acid
0.090	0.034	0 056	0.060	Sulphuric acid
0 074	0.029	0.044	0 060	Lead acetate
0.056	0.029	0 027	0.060	Lead acetate
0.072	0 023	0 049	0 060	Lead acetate
0.074	0 017	0 057	0.060	Control, no H_2S
0.074	0.017	0 057	0.060	Control, no H_2S

The method with sulphuric acid gives results as accurate as can be obtained when there is no hydrogen sulphide present while the results obtained by the use of lead acetate are low.

In order to determine the effect of the addition of sulphuric acid on the

TABLE III.—THE EFFECT OF ADDING SULPHURIC ACID ON THE AMOUNT OF AMMONIA OBTAINED. RESULTS IN PARTS PER MILLION.

	Free ammonia.			Albuminoid ammonia.			Total ammonia.		
Serial No	Ordinary method	Sulphuric acid method	Average.	Ordinary method	Sulphuric acid method	Average	Ordinary method	Sulphuric acid method.	Average
20993	0 010	0 040	0 028	0 088	0.096	0 092	0 104	0 136	0 120
21004	0 024	0 032	0.028	0.072	0.056	0.064	0 096	0.088	0 092
21005	0 048	0.056	0 052	0 112	0.096	0.104	0.160	0.152	0.156
21006	0 024	0 024	0 024	0 064	0 056	0.060	0 088	0.080	0 084
21007	0 120	0.144	0.132	0 432	0.432	0 432	0.552	0.576	0.569
21008	0 080	0.088	0 084	0.144	0.128	0.136	0 224	0.216	0.220
21086	0 544	0.544	0 544	0.288	0.288	0.288	0.832	0.832	0.832
21087	0.864	0.964	0.864	0.160	0.152	0.156	1.024	1.016	1.020
21088	0.144	0.152	0.148	0.104	0.096	0.100	0.248	0.248	0.248

---

[1] *J. Infect. Dis.*, 1904, I, 327.

so-called albuminoid ammonia, a series of waters were analyzed with and without the addition of sulphuric acid. The results of the analyses of nine typical Illinois waters as given in Table III show that the sulphuric acid has no appreciable effect on the amount of ammonia obtained. While the results are not identical, the variations are within the limits of experimental error.

URBANA, ILL.

THE COMPOSITION OF SOME GREEK VASES.

BY WILLIAM FOSTER

Received July 18, 1910.

The purpose of this article is to give an account of some chemical tests made in order to determine the nature and composition of the black glaze of the black-figured and red-figured Attic styles and the red glaze of the Mycenaean style of vases.

This investigation was undertaken at the request of my colleague, Dr. O. S. Tonks, who is interested in Greek pottery from the standpoint of an archaeologist.

Guided by the results of these chemical tests, Tonks has confirmed some of the observations by synthesis, a partial account of which has already been published.[1]

1. Experiments with the Black Glaze.

(1) *Historical Introduction.*—The nature and composition of the fine black glaze on Greek pottery has been a subject of discussion and more or less speculation for many years. As far back as 1761 Caylus,[2] as a result of his investigations, claimed that the glaze was made up of a ferruginous earth, which he classified as manganese. He claimed that this substance baked red, but could be rendered black by an admixture of color, or other earths.

According to Blumner,[3] some later investigators have advanced theories that the materials of the glaze might be graphite and magnesia, that the glaze is made up of an earth but not a metal, and that a combination of the oxides of iron and manganese may have produced the black. Blumner claimed, however, that the real nature of the black color had not been finally determined.

Of the earlier experiments carried out with a view to discover the composition of the glaze, perhaps those of Salvétat,[4] at the Sèvres potteries, are the most worthy of consideration. While Salvétat, in reporting his analysis, did not give any *percentage* of manganese, he claimed that the oxide of manganese is an indispensable component of the composition, and this view is shared in by Brongniart.[1] This the writer hopes to disprove.

---

[1] Tonks, *Am. J. Archaeology,* **12,** 417 (1908)

[2] *Recueil d' Antiquités,* **1,** 86–7.

[3] "Technologie und Terminologie der Gewerbe und Künste bei Griechen und Römern, II, pp. 74ff. The work done up to 1879 is here summarized.

[4] Brongniart, "Traité des Arts Ceramiques," I, pp. 549–52.

Among the later writers, H. B. Walters[2] believes that the problem is still unsolved. He distinguishes between a glaze which was applied to the surface before the application of what he terms the black varnish and the black varnish itself. Birch, Blümner and Brongniart hold views that are somewhat similar. They consider that the glaze and black are different from each other.

Fürtwangler and Reichhold[3] are of the opinion that the black glaze is apparently made up of two parts, namely, a thin, reddish, shining, flowing material and some substance, which, by firing, gives the black. This I do not believe to be likely.

"The nature of the glaze which is to be seen on the finished vase in both the black- and red-figured styles, and the methods of its application, raise puzzling questions about which there is as yet no general agreement."[4]

It is hoped that the following experiments will aid somewhat in solving the puzzle as to the composition of the glaze.

(2) *Experimental.*—Experiments were conducted, in the first place, to find out whether manganese is present as an essential constituent of the glaze, as claimed by Salvétat, or whether its presence is accidental.

Experiment 1.—A fragment of a Greek vase[5] covered with fine black glaze and weighing about 51 grams was placed in a large silver crucible and fused with potassium hydroxide until all the glaze was removed from the clay.[6] The melt thus obtained had a faint greenish tinge, suggestive of a very small quantity of manganese. This melt was treated by the usual methods for the separation of silica and iron, and then hydrogen sulphide was conducted into the ammoniacal filtrate to precipitate any manganese that might be present. A *very* small dirty precipitate was obtained, which, when treated with a borax bead, gave no indication whatever of manganese. This test was confirmed by various other tests. The occurrence of manganese in the glaze must have been *accidental*, therefore, and not an *essential* component of it.

---

[1] *Rev. Archéologique*, **18**, 101 (1891).

[2] "History of Ancient Pottery," I, pp. 214 and 220.

[3] "Griechische Vasenmalerei," Series I, Text p. 19.

[4] Fowler and Wheeler, "Greek Archaeology," p. 429 (1909).

[5] From the American excavations at the Heraeum.

[6] NOTE.—A considerable quantity of the *body* of the vase was necessarily removed at the same time. The writer has tried different methods for removing the glaze, such as chipping it off, and scratching the surface with a fine diamond point; but in all cases the mass of the clay removed from the body of the vase was always much greater than that of the glaze itself. For this reason, since the glaze is exceedingly thin, it was impossible to get enough of the latter for chemical analysis.

Experiment 2.—In the second place, tests were made to find out the amounts of manganese in the black glaze and in the *body* of the vase.

Some fragments of a vase covered with black glaze were treated with a mixture of sulphuric and hydrofluoric acids until all the glaze was removed and disintegrated. After expelling the excess of hydrofluoric acid by repeated evaporations with sulphuric acid, the residue was dissolved in water and nitric acid, and the manganese determined by the colorimetric method of Walters,[1] *i. e.*, by oxidizing the manganese to permanganic acid by means of ammonium persulphate and then diluting in a Nessler cylinder to the mark. The amount of manganese calculated as the oxide (MnO) was 0 06 per cent.

The experiment was repeated with a similar sample taken from the body of the vase. The percentage of manganese was identical (0.06).

The experiment was repeated with a different sample of vase, in this case a diamond point being used to remove the glaze, and 0.04 per cent. of MnO was found in the glaze and also in the body of the vase.

These experiments go to show that the amount of manganese in the glaze is the same as that in the body of the vase. This small amount of the element (average 0.05 per cent) might very well be *accidental*, for it is well known that ordinary clays and rocks containing iron usually contain more or less manganese.

Experiment 3.—It was suspected by the writer that the black glaze might be due primarily to ferrous silicate, therefore the following experiments were carried out to test this hypothesis.

(1) Three grams of a fragment of a vase covered with glaze (the sample was not ground up) were placed in a platinum crucible and treated with a mixture of sulphuric and hydrofluoric acids, great care being exercised to exclude all air. The solution thus obtained was evaporated to dryness, the residue taken up with dilute sulphuric acid, and the ferrous iron determined by means of dilute potassium permanganate. 0.6 cc. of the permanganate were required. The same test was applied to an equal amount of the vase without the glaze. In this case 0.2 cc. of the permanganate was required to oxidize the ferrous iron.

(2) Two grams of a fragment of a vase covered with glaze were crushed to a powder and treated as in (1), the final titration being made with $N/50$ potassium permanganate. Amount of ferrous oxide (FeO) present, 0.50 per cent.

Two grams of the body of the vase were next treated in a similar way. Amount of FeO present, 0.30 per cent.

Several other tests were made, and invariably more ferrous iron was found in the glaze than in the body of the vase.

---

[1] *Chem. News*, 84, 239 (1901); *Proc. Eng. Soc. West. Pa.*, 17, 257 (1901); Hillebrand *Bulletin* 422 (U. S. G. S.), pp. 116–8.

Owing to the fact that it was impossible to get the glaze anything like free from the clay, it was not possible to determine the absolute amount of iron in the ferrous condition in the former; but enough evidence was obtained to indicate that *ferrous iron* (probably as ferrous silicate) is responsible for at least a part of the fine black color of the decorating medium of some of the Greek pottery.[1]

II. Experiments with the Red Glaze of the Mycenaean Style.

If the Greeks employed compounds of iron in the ferrous condition for the production of black glaze, it is reasonable to assume that they employed compounds of the element in the ferric condition to obtain the red glaze, and I dare say that it has been quite generally believed by writers on the subject that iron in the ferric condition had much to do with the production of the red glaze. If this be the case, one would expect to find more ferric iron in the glaze than in the body of the pottery, and less ferrous iron in the glaze than in the body. To test this hypothesis the following experiments were conducted:

Experiment 4.—(1) A fragment of a Mycenaean[2] vase covered with red glaze was found by the analytical method already described to contain 0 44 per cent. of iron calculated as ferrous oxide (FeO). An equal weight of the body of the vase gave 0 56 per cent. of FeO.

A second sample, from another vase, gave 0 35 per cent. FeO in the glaze and 0.43 per cent. in the body, and a third and still different sample gave 0.17 per cent. in the glaze and 0.25 per cent in the body of the vase.

From these experiments it would appear that the body of the pottery covered with red glaze contains more ferrous iron than the glaze—just the opposite of the observation made in the case of the black glaze.

---

[1] Tonks has succeeded, it appears, in confirming these observations by synthesis. He says: "Not to be tedious by enumerating the number of trials I made before getting the desired result, I may say that it proved eventually that a combination of eight parts of nitrate of soda to one of clay, fritted together, and then mixed in the proportions of two parts of frit to one of ferrous oxide, produced a glaze identical with that on Greek vases" (*Amer. J. Archaeology*, XII, 1908, p. 424). Tonks used pipe clay and he claims that if it had been a more fusible variety, the amount of sodium nitrate could have been much less.

It might be objected by some that the Greeks knew nothing about ferrous oxide, inasmuch as the pure compound is a modern preparation of the chemical laboratory. Compounds containing ferrous oxide or iron in the ferrous condition are abundant enough in nature, however, *e. g.*, magnetic oxide of iron, or ferroso-ferric oxide, and ferrous carbonate. Tonks informs me that he has recently succeeded in reproducing the black glaze by the use of the magnetic oxide of iron in place of pure ferrous oxide, but he has not as yet completed his experiments.

[2] Picked up by Tonks at Mycenae. Mycenaean vases were manufactured by the Greeks as far back as 1200–1300 B. C. The other specimens of vases with red glaze experimented on by the author were of the Mycenaean style, but from the Heraeum.

Experiment 5.—The total iron as ferric oxide (Fe_2O_3) was next determined, both in the red glaze and in the body of the clay. The surface of a fragment of vase covered with red glaze was scratched thoroughly with a diamond point and the powder analyzed. Total Fe_2O_3 present, 8.16 per cent. A sample of the same vase without the red glaze contained 7.36 per cent. total iron as Fe_2O_3. After allowing for the ferrous iron, the glaze was found to contain considerably more ferric iron than the body of the clay. A second experiment, on a different fragment of vase, confirmed this observation.[1]

III. Analyses of Mycenaean Vases.

So far as the writer knows, no analyses of Mycenaean pottery have been published. It was thought worth while, therefore, to make a complete analysis of a fragment of a vase of the Mycenaean style, and a partial analysis of another fragment. These results will be given below, and, for the purpose of comparison, the average *approximate* results of the analysis of four fragments of Attic pottery (with black glaze) made in the Harvard University laboratory under the direction of Professor Richards[2] will be given, and also the mean of Salvétat's[3] analyses:

ANALYSES OF ANCIENT POTTERY.

	Fragments of Mycenaean vase. Foster		Fragments of jars and vases (Attic). Widtsoe & Lyon (Harvard Univ.)	Campanian pottery. Salvétat.
Silica (SiO_2)	40 60	47 51	56 10	55 88
Aluminium oxide (Al_2O_3)	17 07	20 40	17.25	18.88
Ferric oxide (Fe_2O_3)	6 93	8 89[4]	8.95	15.80
Ferrous oxide (FeO)	0 56	..	. .	...
Calcium oxide (CaO)	19 80	13 82	5.52	7 48
Magnesium oxide (MgO)	4 42	4.41	5 00	1.63
Potassium oxide (K_2O)	2 96	.	3 26	...
Sodium oxide (Na_2O)	0 21	. .	2.35	...
Carbon dioxide (CO_2)	5 40	2.78	...	...
Water (H_2O)	2 95		2 20	...
	100 90		100 63	

By a comparison of the figures in the different columns, it may be observed that the Mycenaean pottery contains considerably less silica than the Attic and the Campanian. They all contain about the same amount of alumina. The Mycenaean and the Attic appear to contain approximately the same amounts of ferric iron, but the Campanian ware contains about twice as much of this substance. The Mycenaean pottery is *much* higher in lime than the other varieties, and also contains (*i. e.*, the samples analyzed) considerable carbon dioxide. The amounts of magnesia in the Mycenaean and the Attic varieties are nearly equal, but it is considerably less in the Campanian. The potassium oxide is approximately the same in the samples analyzed at Harvard and in the one sample of Mycenaean pottery in which this constituent was determined. While the former contained over 2 per cent. of sodium oxide, the latter contained but a small amount (0.21 per cent.).[1] Owing to the fact that the Mycenaean clay analyzed is low in silica and comparatively high in lime, it should be more fusible. It was observed that in determining the loss of this variety of clay by ignition in a platinum crucible, it melted quite completely.

---

[1] Tonks has been conducting some experiments to confirm these analyses synthetically, and he has already met with considerable encouragement.

[2] Robinson, "Cat. of Greek and Roman Vases," Museum of Fine Arts, Boston, 1893, p. 35.

[3] Brongniart, *op. cit.*, I, p. 550.

[4] Total iron.

CHEMICAL LABORATORY,
PRINCETON UNIVERSITY

CONDITIONS AFFECTING THE ELECTROLYTIC DETERMINATION OF COPPER.

BY W C BLASDALE AND W. CRUESS.

Received August 10, 1910.

Although the electrolytic method for the determination of copper has been in use since 1864, and the literature of the subject is now voluminous, the application of the method to the analysis of ores and metallurgical products often presents difficulties, which are either ignored or but vaguely suggested in the current descriptions of the process. The frequent failures made by students in this laboratory in attempting to use the process have served to emphasize these difficulties, and have led to the series of experiments, the results of which are recorded below. In carrying out these experiments the needs and resources of the practical analyst have been kept constantly in mind.

Effect of Different Forms of Electrodes upon the Rate of Deposition and the Character of the Deposit.

The results obtained with the use of mechanical stirring devices during the last seven years have emphasized the desirability of maintaining a rapid circulation of the electrolyte during electrolysis. It has not been so generally recognized that the circulation of the electrolyte may be increased by taking advantage of the convection currents produced by the gases liberated at the anode or cathode, and by the substitution of Winkler gauze electrodes for those of the Mansfield type.[2] It seems probable that the relative efficiencies of the different forms of stationary electrodes depend almost entirely upon the extent to which they favor circulation of the electrolyte, and the equal distribution of the current density over the entire surface of the cathode.

---

[1] Chemical analyses of the different varieties of clay used by the ancient Greeks are still too inadequate to throw much light on the manufactures of different localities.

[2] See, however, the Benner article, p. 1231.—EDITOR.

In order to obtain definite data upon this point the rates of precipitation of known amounts of copper under identical conditions, except as regards the electrodes used, were determined. Each of the solutions contained exactly 0 1975 g. of copper as sulphate, 2 cc. of concentrated sulphuric and one of concentrated nitric acids, and water to make 140 cc. They were electrolyzed with a practically constant current of 0.34 ampere and the copper deposited during definite time intervals determined. Except where Classen dishes were employed, the stand to which the electrodes were attached was raised at the end of the desired time interval, and the electrodes plunged in a beaker of water, the current allowed to run for some three minutes longer, after which the cathode was removed, washed in two changes of alcohol and dried and weighed. It was shown, both by determining the rate of action of solutions of this composition on recently precipitated copper, and by testing the washings of the electrodes that this method of removing the cathode involves no recognizable error, it is extremely rapid and convenient.

The cathodes used in the various experiments were as follows:

A. A Classen dish of 200 cc. capacity, with 140 cc. of electrolyte; this gave an available surface of about 120 sq. cm The anode used with it consisted of a disk of foil with six radially distributed openings near its rim; it was 4.1 cm. in diameter, and was suspended by a stout wire in the center of the dish, slightly below the level of the liquid retained by the latter.

B. A cylinder of foil 2 5 cm. in diameter and 5 cm. in length welded to a supporting wire one mm. in diameter and 12 cm. in length. The total area exposed to the solution was 79 sq. cm. The anode used was a cylindrically coiled spiral of platinum wire suspended in the center of the cylinder. Both electrodes extended nearly to the bottom of the beaker containing the solution; the beaker used was approximately 5 5 cm. in internal diameter.

C. A cylinder of the same dimensions as B, but pierced with 270 holes one mm. in diameter, distributed at approximately equal intervals over its entire surface. The anode and containing vessel were of the same form and size as with B.

D. A cylinder of gauze 3.2 cm. in diameter and 5.5 cm. in length, the gauze composed of platinum wire 0.06 mm. in diameter, with 41 meshes per linear cm. The cylinder was supported by a wire 0.54 mm. in diameter and 13 cm. in length. Assuming that the entire surface of the wire composing the gauze was in contact with the solution, its available area was 93 sq. cm. The anode and containing vessel were the same as those used with B.

E. A cylinder of gauze of the same form and dimensions as D. The anode, however, consisted of a stout wire coiled to form a horizontal spiral, suspended at the bottom of the containing vessel. This was of the same dimensions as with B.

F. A cylinder of gauze 4 cm. in diameter and 4 cm. long; the gauze composed of wire 0.1 mm. in diameter with 25 meshes per linear cm. This was supported by a wire 1 mm. in diameter and 12 cm. long. The calculated surface area was 80 sq. cm. The anode and beaker used were of the same form and dimensions as with B.

The results obtained with these electrodes are shown in part in the series of curves of Plate 1, in which the abscissas represent time in minutes, and the ordinates the copper deposited, in milligrams. The superiority of the gauze electrode D over all others is at once apparent. Its efficiency is due to the fact that it interposes almost no obstacle to the development of convection currents, the direction and intensity of which are easily observed by placing a few mg. of precipitated silica in the solution. It can be shown by this device that the gas liberated at the anode is here distributed over a limited area and produces a current of considerable intensity, which draws the solution through the meshes of the cathode from the periphery. Where foil electrodes are used there is but little interchange of solution between the annular space surrounding the cathode and the cylindrically bounded area within. Further, while the current density is nearly equally distributed over the entire exposed surface of the gauze cathode, it is much greater on the inside than the outside of the foil electrodes, and it is easy to show that only a small percentage of the copper deposited on electrodes of this style separates on the outside of the cylinder.

A comparison of the results obtained with D and F shows that the efficiency increases somewhat with the fineness of the mesh and the wire of which the electrode is composed. This, taken together with its extreme lightness and consequent low cost, places D at the head of the list as regards economy. Although D was somewhat fragile and had to be handled more carefully than F, two such electrodes have been in general use for over three years and are still in good order.

A comparison of the results obtained with B and C show that by providing a number of openings in the foil composing the cathode the efficiency is appreciably increased, but the superiority of the gauze form still remains most striking.

A comparison of the results obtained with E and D shows that the cylindrical form of anode possesses a slight advantage over the disk form. This is due to the distribution of the liberated gas over a greater horizontal area. Still another difficulty arises from the fact that much of the liberated oxygen comes in contact with the precipitated copper and may produce an appreciable amount of oxidation; dark deposits were frequently obtained wherever the disk form of anode was used. With this exception the deposits obtained in the entire series of experiment were satisfactory. A comparatively small increase in the amperage used gave poor deposits where foil electrodes were used.

The comparative efficiencies of the different forms of electrodes used are summarized in the following table, in which the last column represents the time needed for the precipitation of 0.1975 g. of copper to within ±0.02 mg.

	Cathode used.	Surface exposed.	Wt. in g	Time needed. Minutes.
A	Classen dish . .	120	38	400
B.	Mansfield	79	11.0	450
C.	Mansfield with holes	78	11.0	390
D.	Winkler	93	4.2	50
E.	Winkler..	93	4.2	60
F.	Winkler .	80	9.4	100

Effect of Varying Amperage upon the Rate of Deposition.

If all the current which passes through the solution were carried by the ionized copper salt the rate of precipitation would be directly proportional to the amperage. In practice other electrolytes are always present and carry more or less of the current. The electrolysis of neutral salts yields free acids, and acid is usually necessary to prevent the separation of other metals present. So long as the decomposition voltage of the copper ions is somewhat smaller than that of the other cations present, and so long as their concentration is sufficiently large as compared with the amperage used, the greater part of the positive current will be carried by them, but as their concentration decreases the proportion of the positive current carried by them must rapidly decrease and finally become zero. Rapid circulation of the solution brings larger numbers of copper ions within the sphere of attraction of the cathode within a given time interval, and increases the proportion of positive current carried by the copper ions during the later stages of the deposition. Increasing the amperage not only increases the rate of deposition directly, while the solution contains a comparatively high concentration of copper ions, but also indirectly by increasing the circulation of the solution through the gases liberated at the anode and cathode.

In order to determine the actual effect of varying current strength the rates of precipitation were determined under identical conditions except as regards amperage. The solution used contained 0.1975 g. of copper as sulphate, 2 g. of ammonium nitrate, 4 cc. of concentrated nitric acid and water to make 140 cc The gauze electrode D was used throughout. The curves 1, 2, 3, 4, and 5, shown on Plate II, represent the results obtained where currents of 0.19, 0.34, 0.5, 0.78 and 5.5

amperes, respectively, were used. The details of manipulation were the same as in the previous series of experiments. In all but the last series the amount of copper finally obtained differed from the correct amount by less than 0.3 mg.; when 5.5 amperes were used the solution attained a temperature of 60° and the solvent action of the large amount of nitric acid present was so great that the final result was 1.2 mg. low. This loss was due in part to copper in the wash water and in part to copper left in the original solution. The depolarizing action of the large concentration of nitrate ions present was sufficient to prevent the liberation of hydrogen even with the highest currents used. The deposits were all dense and compact; those obtained with the higher amperage showed a slight tinge of brown in place of the normal red color.

It might be noted here that some experiments by Stoddard,[1] which involved the use of a gauze cathode, a volume not exceeding 50 cc., and the presence of only one cc. of nitric acid, gave more rapid precipitation than that here noted. His work has been criticized by Price and Humphreys,[2] who found the time needed under similar conditions somewhat greater than that used by Stoddard.

Effect of Varying Concentrations.

The proportion of positive current carried by copper ions in a series of solutions containing the same amount of copper salt should be greater,

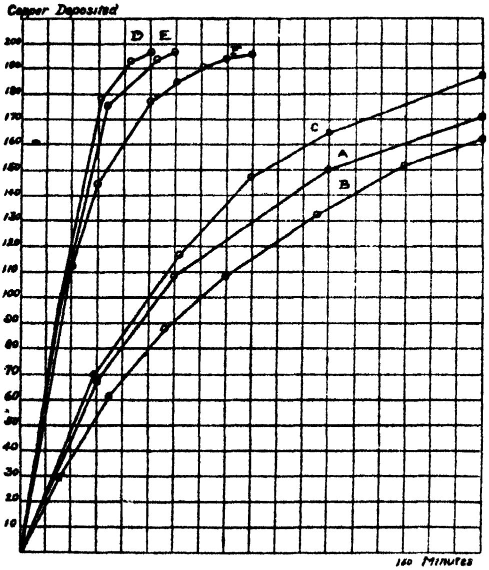


Plate I.—Results with varying types of electrodes.

---

[1] This Journal, 31, 385 (1909).

[2] *J. Soc. Chem. Ind.*, 29, 307 (1910).

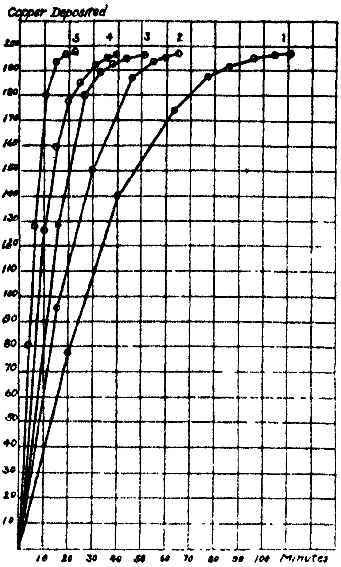


Plate II.—Results with varying current strengths.

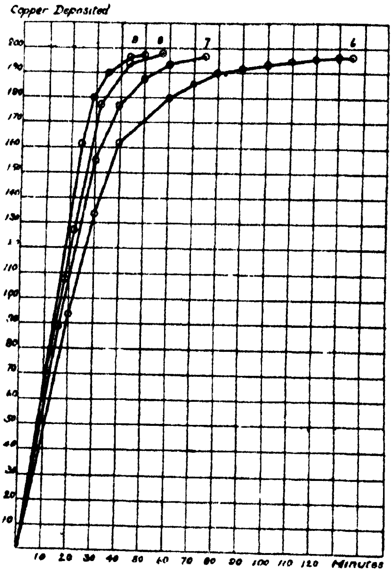


Plate III.—Results with varying concentration.

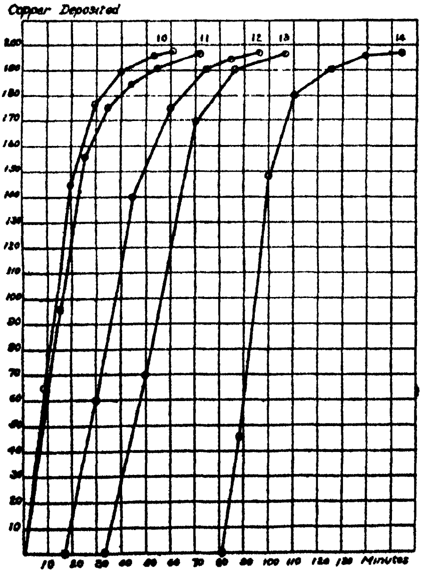


Plate IV.—Results with varying amounts of iron.

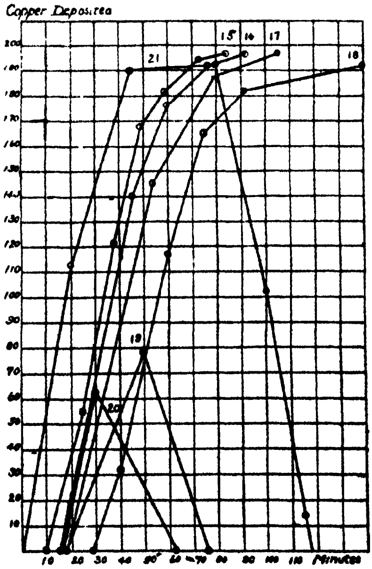


Plate V.—Results with varying concentrations of iron and nitric acid.

especially as the deposition approaches completion, with solutions of high than with those of low concentration. The importance of this factor has been shown by Richards,[1] although the method which he recommends for effecting the precipitation is scarcely feasible in routine analytical work.

Some data showing the effect of varying concentration on the speed of precipitation are represented by curves 6, 7, 8 and 9 of Plate III. The solutions used contained 0.1975 gram of copper as sulphate and were diluted to 70, 140, 210 and 280 cc., respectively. They contained nitric and sulphuric acids corresponding to a concentration of one cc. of the former and two of the latter, for each 140 cc. of total solution. The gauze electrode D and a current of 0 34 ampere were used in all cases, but the size and form of the beakers containing the solutions were necessarily changed somewhat from those used in the previous experiments.

The curves show that the time interval during which the rate of precipitation remains practically constant increases greatly with the concentration. Even when the volume is 140 cc. this rate remains practically constant till 90 per cent. of the copper present has been precipitated; beyond this point the rate decreases rapidly. With larger volumes the change in rate occurs earlier and becomes increasingly greater with the larger volumes. This may be taken to mean that up to the point at which the rate shows a decided change the current is carried entirely by the copper ions; beyond this point it is carried to an increasing extent by the hydrogen ions. The final form of the curve is the net effect of the actual change in concentration and the change in stirring efficiency of the anodic gas, owing to the increased volume of liquid to be stirred.

Amount and Nature of Acid Present.

Although copper is readily separated by the electric current from neutral or alkaline solutions, the application of this method to the analysis of ores almost invariably demands the presence of a slight concentration of hydrogen ions. If sulphuric acid is used, and if the cathode consists of a Classen dish or a foil, the current density must be kept low or the deposits are spongy. The difficulty becomes increasingly large as the concentration of the copper ions decreases, and can be remedied, as shown by Richards,[2] by making reductions in the current strengths as the deposition progresses. Rapid circulation largely overcomes the difficulty, since larger numbers of copper ions are thereby rendered available for the transport of the current and virtually increase their effective concentration. A somewhat extended experience has convinced us that this difficulty is reduced to a negligible factor by the use of gauze electrodes. We have not yet obtained a spongy deposit where these electrodes were used. This has been noted and used by Förster.[1]

---

[1] THIS JOURNAL, 26, 530 (1904).

[2] *Loc. cit.*

Where a sufficient concentration of nitrate ions is present, the danger of obtaining spongy deposits is small, but another difficulty arises from the formation of brittle, crystalline aggregates, which grow out from the lower edge of the cathode, and sometimes at the point where the sustaining wire emerges from the solution. Apparently this difficulty is also avoided by sufficient circulation of the solution, for it has not been noted where the solution was stirred, or where a gauze cathode was used.

Differences in the comparative solvent action of the two acids on precipitated copper might be expected to affect the rate of precipitation and the difficulty of removing the cathode from the solution without resolution of appreciable amounts of the precipitate. The amount of copper dissolved from a copper-coated gauze cathode by dilute solutions of these acids during a definite time interval was found to vary greatly, but in every instance the action of the nitric acid was much greater than that of the sulphuric acid, and was increased to a much greater extent by increasing the temperature to 60°. In one instance 78 mg. of copper were dissolved by a solution containing 2 cc. of nitric acid per 140 and heated to 60°. The precipitation of the last few milligrams of copper from such solutions is not easily effected and we have not found either the rotating anode or the gauze cathode satisfactory where the solution was heated either externally, or internally by the current. The residual solutions usually showed the presence of copper by the ferrocyanide test, and occasionally faint traces of the same could be detected in the wash water. Where currents of five or more amperes are used, nitric acid should not be present, except in small concentrations.

If the temperature of the solution does not rise above 30° the concentration of the solution with respect to copper is easily reduced below the point recognized by the ferrocyanide test, even where the concentration amounts to as much as 4 cc. of either acid per 140 cc. of solution. The time needed for complete precipitation from such solutions is practically the same, though the rate at which the last ten milligrams are precipitated is slightly less with the larger concentrations of nitric acid.

Effect of Iron Salts upon the Rate of Precipitation.

A. In the Absence of Nitrate Ions.—The curves plotted on Plate IV show how the rate of precipitation is affected by the presence of iron salts. The solutions used contained in every instance 0.1975 g. of copper as sulphate, and 2 cc. of concentrated sulphuric acid, and were diluted to 140 cc.; they were electrolyzed with the gauze electrode D, using a current of

---

[1] *Z. angew. Chem.*, 19, 1848 (1906).

0.34 ampere. The curve numbered 10 represents the results obtained where no iron was present; No. 11, where the solution contained 0.8 g. of iron as ferrous sulphate. The comparatively large amounts of ferrous ions present reduced perceptibly the normal rate of precipitation during the later stages of the deposition, but did not otherwise affect the precipitation.

The results represented in curves numbered 12, 13 and 14 represent the results obtained with solutions containing respectively 0.2, 0.4 and 0.8 g. of iron as ferric sulphate. They show that no copper is deposited for a definite interval, which is roughly proportional to the amount of ferric salt present. A similar series of solutions were electrolyzed under the same conditions and titrated with a solution of potassium permanganate, at the point at which the copper first began to separate. The results showed that the appearance of the deposit was correlated with the reduction of the concentration of the ferric ions to an approximately fixed value. Evidently we are here dealing with a complex equilibrium in which the important factors are the strength of the current used, the concentration of the ferric ions, and the reaction constant of the equation

$$2Fe''' + Cu \longrightarrow Cu'' + 2Fe''.$$

The value of this constant is evidently large, for if a copper-coated electrode is allowed to stand in a solution of a ferric salt till equilibrium is attained, the concentration of the resulting solution with respect to ferric ions is reduced almost to zero. By titrating still another series of solutions it was shown that the reduction of the iron progresses during the deposition of the copper and was completed before the copper was all deposited.

B. In the Presence of Nitrate Ions. General Phenomena.—The curves plotted on Plate V show the effect upon the rate of precipitation of varying combinations of ferric salts and nitric acid. The solutions contained in all cases 2 cc. of concentrated sulphuric acid and water to make 140 cc. and were electrolyzed with the gauze electrode D, using a current measuring 0.34 ampere. In 15 the solution contained 0.2 g. of iron as ferric sulphate and no nitric acid; in 16, 17, 18 and 20 they contained 1, 3, 4, and 5 cc., respectively, of concentrated nitric and 0.2 g. of iron as ferric sulphate; in 21 it contained 0.2 g. of ferrous sulphate and 4 cc. of concentrated nitric acid; in 18 it contained 0.4 g. of iron as ferric sulphate and 3 cc. of concentrated nitric acid. In some cases only a few points on the curves were determined and the exact position of the maxima is only approximately represented. The extreme rapidity with which the resolution sometimes took place, and the difficulty of accurately controlling all the factors concerned, especially the temperature, make accurate determinations difficult; an approximate accuracy is all that the present work requires.

The curves show that so long as the concentrations of both nitrate ions and ferric ions are kept low, the rate of precipitation is merely retarded, but where either of these factors, especially the nitrate concentration, becomes large, deposition may take place normally up to a certain stage, then a rapid resolution of the deposited copper. This phenomenon is well known to analysts, who have had much experience in applying the electrolytic method to the analysis of pyritiferous ores and has been described by Larison[1] and by Farlie and Boone.[2]

Probable Cause of the Phenomenon.

The rapidity with which the process of resolution takes place, and the fact that with a constant amperage it may not take place at all until a large amount of the copper has been precipitated, make it improbable that either nitric or sulphuric acids or ferric salts are the effective agents concerned. Its frequent association with the blackening of the solution (presumably due to the nitroso compound of ferrous sulphate) suggests that the action is due to the presence of one or more of the products resulting from the reduction of nitric acid.

A systematic study of the action of solutions of nitric acid containing the various lower oxides of nitrogen has led to the conviction that nitrous acid is the reagent which is chiefly concerned in this phenomenon, though nitric oxide may play some part in it. Some of the data upon which this statement is based are as follows.

(*a*) The copper in a solution containing 0.5 g. of copper sulphate, 2 cc. of concentrated nitric acid and water sufficient to make 100 cc. was deposited on a gauze electrode. The latter was then removed and after saturating the solution with nitrous oxide gas was again placed in the solution. The amount of copper dissolved at the expiration of forty minutes was 0.017 g.

(*b*) A solution and electrode prepared exactly as in (*a*) were saturated with nitric oxide gas (prepared from copper turnings and nitric acid). The amount of copper dissolved from the cathode by this solution at the expiration of forty minutes was 0.074 g.

(*c*) A solution and electrode prepared exactly as in (*a*) were partly saturated with nitrogen peroxide prepared from tin and nitric acid. The copper-coated cathode immersed in this solution for forty minutes lost 0.140 g.

(*d*) A solution was prepared which contained 2 cc. of concentrated nitric acid and 2 cc. of a solution saturated with respect to both ferrous sulphate and nitric oxide, and water sufficient to make 100 cc. The copper-coated cathode lost 0.007 g. as the result of immersion in this solution for forty minutes.

---

[1] *Eng. Min. J.*, 84, 442 (1907).

[2] *Electrochem. Met. Ind.*, 6, 58.

(*e*) A solution prepared as in (*a*) was treated with a mixture of nitric oxide and nitrogen peroxide (prepared from starch and nitric acid). The entire amount of copper on the cathode, that is, 0.1975 g., was dissolved within five minutes.

Recognizing the fact that nitrogen peroxide in contact with water immediately forms a mixture of nitrous and nitric acids, and that the nitric oxide prepared from copper and nitric acid probably contained appreciable amounts of the peroxide, it seems probable that the phenomenon under discussion is mainly due to the presence of nitrous acid. It has been clearly shown by Millon,[1] Veley[2] and others that this acid has a pronounced catalytic action on the dissolution of copper in nitric acid. There is also reason to believe that the acid itself has a remarkable solvent action on the metal. A one-tenth normal solution of potassium nitrite acidified with an equivalent amount of sulphuric acid dissolved 0.1 g. of deposited copper in five minutes, liberating a large amount of nitric oxide gas. A half-normal solution also acidified in like manner dissolved 0.14 g. in three minutes. Its action is much greater than that of corresponding concentrations of either sulphuric or nitric acids. There is nothing surprising in this statement. If it is true that the dissolution of copper by nitric acid depends first upon the comparatively high dissociation constant of nitric acid, and second upon the ability of nitrate ions to reduce the concentration of the liberated hydrogen to an exceedingly small value, it would not be surprising to find a still greater effect with nitrous acid. The latter acid may possess a slightly smaller dissociation constant, but it is probable that the nitrite ions are more efficient in reducing the concentration of the liberated hydrogen than the nitrate ions.

Formation of Nitrous Acid during Electrolysis.—That nitrous acid is actually produced during the electrolysis of solutions containing sufficient concentration of nitric acid and a ferric salt can be shown by titrating such solutions with potassium permanganate. Thus by electrolyzing a series of solutions, all containing 0.196 g. of copper, 0.1753 g. of iron as ferric sulphate, two cc. of concentrated sulphuric and three of concentrated nitric acids, and water to make 140 cc., for definite time intervals, weighing the precipitated copper and titrating the residual solution, the following results were obtained:

Time interval. Minutes.	Weight of copper deposited.	Reducing power of soln. Fe.
60	0.1762	0.1574
90	0.1925	0.1939
120	0.1946	0.2441
180	0.1958	0.2112

---

[1] *J. prakt. Chem.*, 29, 338.

[2] *Proc. Roy. Soc., London* 48, 458.

Although the current strength here used was sufficient to prevent any recognizable re-solution of the precipitated copper, it is interesting to note that the rate of precipitation after ninety minutes had elapsed, even for the low concentration of copper concerned, was far below the normal value.

The exact conditions necessary for the formation of nitrous acid and the mechanism of the reaction have not yet been determined and we have never obtained evidence of the formation of nitrous acid in the electrolysis of copper nitrate solutions containing free acid unless an appreciable concentration of an iron salt was present. Apparently also a low concentration of hydrogen ions favors the formation of it. We offer no theory of the mechanism of the reaction.

The Use of Urea in Destroying Nitrous Acid.—It has been shown repeatedly that the addition of a sufficient amount of urea to solutions in which re-solution of the precipitated copper had taken place, resulted in the liberation of a large amount of gas and prompt precipitation of the entire amount of copper. It was further shown that the addition of urea to solutions containing several cc. of nitric acid before electrolysis is started will often permit of complete deposition of the copper, whereas in an exactly parallel test, in which the urea was omitted, complete deposition was impossible. The rate of precipitation is, however, still lower than normal, even where 5 g of urea per 100 cc of solution are used, which means presumably that this reagent is still unable to reduce the concentration below a value which affects the normal rate of precipitation to an appreciable extent.

Since entirely satisfactory deposits can be obtained with the gauze electrode in the entire absence of nitrate ions, it is undoubtedly preferable to electrolyze solutions of ores containing only copper and iron in he presence of sulphuric acid only. When it becomes necessary to separate copper from solutions containing both iron and nitric acid, urea may be added with advantage, to prevent the accumulation of undesirable concentrations of nitrous acid in the solution.

Effect of the Presence of Arsenic.

Where solutions containing a salt of copper and arsenic acid are electrolyzed mere traces of arsenic are often separated during the deposition of the copper; larger amounts may separate after most of the copper has been precipitated, and is then easily recognized by the smoky color which it imparts to the precipitate, or if large amounts have separated, by its loosely adherent character and black color. Several devices have been used to avoid the resulting error.

Solution of the precipitate in nitric acid and reprecipitation from a solution containing a reasonable amount of nitric acid can be depended on to give good results in practically all cases.

The removal of mere films of arsenic from the surface of the cathode by carefully heating the latter over a gauze often gives good results, but is not entirely reliable, owing to the difficulty of entirely avoiding oxidation.

Attempts to separate the two metals by the constant voltage method we have found unsatisfactory, even where low amperages were used and is incompatible with the rapid methods of precipitation.

The addition of oxidizing agents for the purpose of keeping the arsenic in the pentavalent form has been generally recommended. Hollard[1] claims that the addition of ferric sulphate effects the desired object, but as the iron is itself reduced during the electrolysis, this seems improbable, and we find that the electrolysis of solutions containing arsenic acid and a ferric salt, in addition to copper, give large deposits of arsenic, provided the solution contains no nitrate ions. Since the solution used by Hollard contained nitric acid, we attribute his success to the latter reagent. The exact concentrations of nitrate ions necessary to prevent precipitation of arsenic depend on the concentration of the latter and upon many other factors. We find that where the solution has a volume of 100 cc. and contains 2 cc. of concentrated sulphuric acid and 50 mg. of arsenic, separation of the latter is effectually prevented by the presence of 5 g. of ammonium nitrate, even though the current is allowed to pass through the solution for several hours after the copper, also present, was deposited. Under similar conditions one cc. of concentrated nitric acid prevented the separation of arsenic from a solution containing 10 mg. of the latter. These results were obtained with the gauze cathode using currents of as much as 0.75 ampere. The limits given are only the roughest kind of approximations.

Effect of the Presence of Salts of Zinc and Aluminium.

The addition of either zinc or aluminium to the extent of 0.4 g. has but little effect on the time needed for complete deposition of copper. The solutions used in determining this fact contained only sulphates and sulphuric acid, and were electrolyzed with the gauze electrode, using 0.34 ampere. A very slight decrease in the rate at which the last four mg. were deposited was noted, which increased the time needed by about five minutes.

A second effect has been observed in the electrolysis of solutions containing large amounts of zinc in addition to copper with electrodes of the Mansfield type, namely, a greater tendency for the formation of unsatisfactory deposits. These effects were never observed where gauze electrodes were employed.

---

[1] *Analyse des Metaux par Electrolyse*, 83.

Effect of the Presence of Lead Salts.

This element may separate in large amounts with the copper from solutions containing sulphuric acid. A large concentration of nitrate ions prevents this, but the amount needed is in excess of that which is desirable, if iron is also present in large amounts. As most of the lead present as ore is usually changed into the sulphate, in preparing the solution, it is preferable to use sufficient care to separate it as completely as possible in this form. We find that, if the insoluble precipitate of the sulphate is left in contact with the solution, very large amounts may be dissolved and precipitated as the deposition progresses.

Practical Application to the Analysis of Ores.

The data presented in the previous sections indicate the difficulties to be avoided in applying the electrolytic method to the analysis of pyritiferous ores. If one-gram samples of such ores are used the resulting solutions may possibly contain 0.2 g. of copper, 0.4 g. of iron and variable amounts of zinc, arsenic and lead.

Assuming first that arsenic is not present and that lead has been carefully removed as sulphate, it should be possible to separate all the copper by the use of the Winkler electrode and a current of 0.75 ampere within ninety minutes, provided the volume does not exceed 100 cc. and the solution does not contain more than five cc. of concentrated sulphuric and no nitric acid. To test the suggestion, a series of solutions containing 0.1956 g. of copper and 0.4 g. of ferric iron were electrolyzed under the conditions named, using the gauze electrode F. The results obtained were:

0.1957 0.1957 0.1958

Assuming that arsenic is also present, either the solution should be electrolyzed under the conditions named above, the deposit dissolved in nitric acid and re-electrolyzed; or, where the amount is small, good results might be expected from a single precipitation by adding to the solution from one to two cc. of nitric acid and 5 g. of urea. To test this suggestion, a series of solutions containing 0.1956 g. of copper and 0.4 g. of ferric iron and 0.01 g. of arsenic (added in the form of H_3AsO_4) were electrolyzed as before, after the addition of one cc. of nitric acid and 5 g. of urea. The results obtained were:

0.1959 0.1948 0.1957 0.1959

CHEMICAL LABORATORY,
UNIVERSITY OF CALIFORNIA

NOTE.

New Normal Solution and Reagent Bottle.—The new normal solution bottle which I have designed is the simplest and most effective of any that has come under my notice. The bottle is of the long narrow type, having a ground-glass cap. The cap and bottle are each provided with a groove which, when turned to coincide, allows the free entrance of air, while when turned in any other position forms an air-tight seal.

Into the bottle are drilled two small holes, one at the upper portion, the other near the bottom. A burette is procured whose delivery tube is bent at two right angles (or an ordinary burette which has been bent into this form). At the base of this burette an opening is blown, right in line with the graduated tube. To this opening a piece of glass tubing which is provided with a glass stopcock, and also has been bent at right angles, is fused. To the top of the burette another piece of glass tubing which has also been bent at right angles, is fused. The two ends which are now at right angles with the burette, and pointing in directly opposite direction from the delivery tube, are placed in their respective holes in the bottle and fused.

The support for the bottle is a light wooden frame, which in turn is suspended between two triangular racks by trunions, which allow the bottle free motion backward and forward. The bottles are never removed from these frames. When refilling is necessary the frame is lifted from its bearings and when the bottle is filled the frame is set back into position. On the base of each stand, between the triangular supports, a piece of white tile is fitted on which the titration is performed.

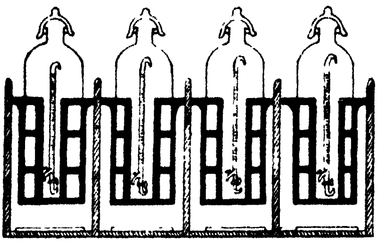


FIG. 1.

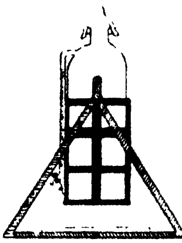


FIG. 2.

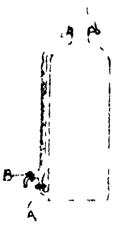


FIG. 3

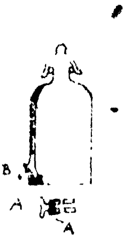


FIG. 4

In order to manipulate the bottle stopcock *A* (Fig. 3) is opened, stopcock *B* closed, the grooves in the cap and neck are brought to coincide, the bottle is then grasped by the neck and tilted forward, which allows the solution to flow up into the burette. Stopcock *A* is then closed while the bottle is still in its inclined position, preventing the solution from passing from the burette back into the bottle, the bottle is then allowed to regain its original upright position, and the burette is ready for operation. These bottles are arranged in series, as shown in Fig. 1, which is very convenient and requires very little space.

The new reagent bottle, as shown in Fig. 4, is constructed in the same manner as the normal solution bottle, excepting that the burette is part of the bottle and stopcock *A* is set into the bottle, allowing the bottle to be handled as any ordinary reagent bottle, as well as supplying a long-felt necessity, that of knowing the amount of reagent one is using either in qualitative or quantitative work, without going to the necessary trouble of using cylinders, pipettes, etc. One is also positive that no other reagent or dirt of any kind has come in contact with the measuring apparatus.

This bottle is manipulated in the same manner as the normal solution bottle, only held in the hand instead of a support. FRANK M. DAVIS.

MACANDREWS AND FORBES CO.,
CAMDEN, N. J.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

METATHETICAL REACTIONS: ETHER-THIOUREAS AND THEIR RELATION TO PSEUDOAMMONIUM BASES.

BY TREAT B. JOHNSON AND HERBERT H. GUEST.[1]

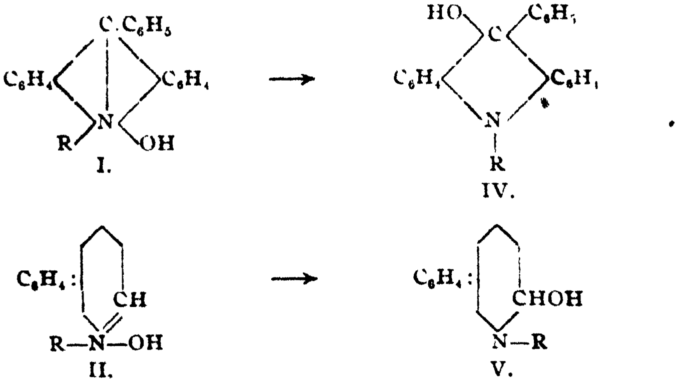
Received June 18, 1910.

Contents.

I. Pseudoammonium Bases and Their Alcoholates. II. Ether-thioureas and Their Behavior towards Alcohols. III. Experimental Part

I. Pseudoammonium Bases and Their Alcoholates.

A characteristic feature of cyclic, quaternary bases (ammonium bases) is their tendency to undergo isomerization in aqueous solution. The hydroxyl group of the base migrates from nitrogen to a carbon atom, giving trivalent-nitrogen compounds or pseudoammonium bases (*ψ-ammonium bases*).[2] Decker calls these rearrangement products *oxydihydro* or *carbinol* bases.[3] These transformations in the acridine (I), quinoline (II) and isoquinoline (III) series are represented by the following formulas:

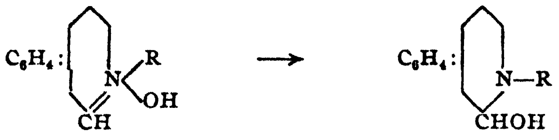


---

[1] Presented at the San Francisco meeting of the American Chemical Society.

[2] Hantzsch and Kalb, *Ber.*, 32, 575, 3109.

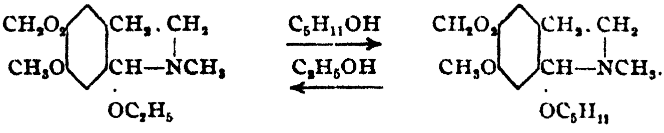
[3] *Ber.*, 25, 3327.



III. VI.

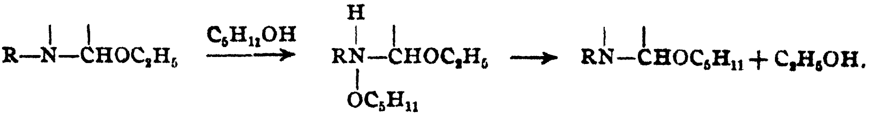
The pseudoammonium bases IV, V, VI (pyridines, quinolines, isoquinolines and acridines) are especially characterized by their behavior towards alcohols. They react at ordinary temperature, with loss of a molecule of water, giving alcoholates or ethers (Sauerstoffäther)[1] which are capable of undergoing unique transformations when warmed with alcohols. The characteristic behavior of these cyclic alcoholates is summarized in the following quotation from a paper by Decker[2] on the alcoholates of some quinoline pseudoammonium bases:

"Gegenüber Alkoholen mit anderen Radikalen verhalten sich die Alkoholate in der Weise, dass sie ihren an Sauerstoff gebundenen Alkylrest leicht und glatt gegen den Rest des in Überschuss angewandten anderen Alkohols umtauschen. So wurde das Methylalkoholat in einem Überschuss von Benzylalkohol unter Erwärmen gelöst und nach erkalten krystallisirte das characteristische Benzylalkoholate heraus." Kuntze,[3] for example, has recently shown that ethoxyhydrocotarnine (VII) and *l*-amoxyhydrocotarnine (VIII) react with *l*-amyl and ethyl alcohol, respectively, on warming, with transposition of their alkyl groups.



VII. VIII

Two theories have been advanced to explain the mechanism of this reaction of an alcoholate with alcohols. According to Decker[4] the alcohol first adds to the nitrogen atom of the alcoholate giving an unstable addition product, which then loses a molecule of alcohol giving a new alcoholate. This change involves necessarily a rearrangement of an alkoxy group from nitrogen to the carbon atom. These changes are represented by the following formulas:



$$R{-}\overset{|}{N}{-}\overset{|}{C}HOC_2H_5 \xrightarrow{C_5H_{11}OH} R\underset{\underset{OC_5H_{11}}{|}}{\overset{\overset{H}{|}}{N}}{-}\overset{|}{C}HOC_2H_5 \longrightarrow R\overset{|}{N}{-}\overset{|}{C}HOC_5H_{11} + C_2H_5OH.$$

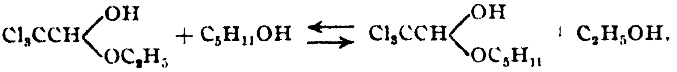
[1] Roser, *Ann.*, 254, 362. Freund, *Ber.*, 22, 2337. Decker, *Ann.*, 254, 360. *Ber.*, 25, 3327; 33, 1715. Freund and Bamberger, *Ber.*, 25, 1753.

[2] *J. prakt. Chem.*, 45, 182. See also *Ber.*, 25, 3327.

[3] *Arch. Pharm.*, 246, 110 (1908).

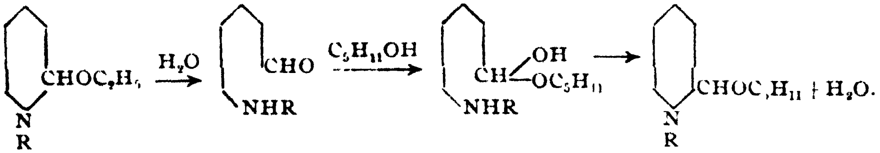
[4] *Ber.*, 33, 1715.

Gadamer[1] takes issue with Decker[2] and interprets these transformations of quinoline and isoquinoline alcoholates by typical, aldehyde reactions. According to him, the reaction is perfectly analogous to the action of alcohols on chloral alcoholates.[3] He assumes that the cyclic



$$Cl_3CCH\begin{matrix}OH\\OC_2H_5\end{matrix} + C_5H_{11}OH \rightleftarrows Cl_3CCH\begin{matrix}OH\\OC_5H_{11}\end{matrix} + C_2H_5OH.$$

alcoholates undergo partial dissociation in solution into alcohol and an aldehyde base. The latter then reacts with the alcohol in excess, by mass action, giving an aldehyde alcoholate, which then condenses to a new alcoholate of the pseudobase. These changes are represented by the following formulas:



He writes:[4] "Jedenfalls ist die Auffassung Deckers bezuglich der Ueberführung eines Alkoholates in ein anderes nicht haltbar. Man massenwirkung annehmen müssen. Diese setzt aber veraus, dass die Alkoholate in Aldehydbase und Alkohol dissoziiert sind."

The mechanism of these characteristic, metathetical reactions is still a subject of polemic. Therefore, with the possibility of obtaining new data which might contribute to our present knowledge of these transformations, it seemed desirable to investigate the behavior, towards alcohols, of some acyclic nitrogen compounds related in structure to cyclic pseudoammonium alcoholates. We selected, therefore, for our study some representatives of a new class of thioureas—*ether-thioureas*—recently described in this laboratory.

II. Ether-thioureas and Their Behavior towards Alcohols.

In a previous paper from this laboratory, the writers[5] have shown that certain primary halogen-ethers (IX) react smoothly with potassium thiocyanate giving isothiocyanates (X). We described isothiocyanodimethyl-, isothiocyanomethylethyl- and isothiocyanomethylisoamyl ethers and also several representatives of a new class of thioureas—*ether-thioureas* (XI). The latter were obtained by the action of these isothiocyanates on organic bases.

$RO.CH_2Cl$	$RO.CH_2NCS$	$ROCH_2NHCSNHR'$
IX.	X.	XI.

($R = CH_3, C_2H_5$. $R' = C_6H_5$, etc.)

---

[1] *Arch. Pharm.*, 243, 12; 246, 89. Gadamer and Kuntze, *Ibid.*, 246, 91.

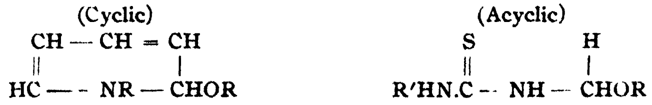
[2] *Loc. cit*

[3] Kuntze, *Loc. cit.*

[4] *Arch. Pharm.*, 246, 96.

[5] *Am. Chem. J.*, 41, 337 (1909).

If a comparison is made of the structural formula of a pyridine alcoholate with that of an ether-thiourea, the fact is revealed that the thiourea and cyclic derivative are very closely related. In fact, the thiourea contains the same linking $=\underset{|}{C}.\underset{|}{N}.\underset{|}{CH}.OR$ as the cyclic alcoholate, and may be regarded as an acyclic pseudoammonium compound. These thioureas, therefore, might be expected to undergo transformations with alcohols analogous to those which have been observed to take place with the cyclic alcoholates. Our observations have confirmed such an assumption.



$(R = CH_3, C_2H_5.\ R' = C_6H_5, C_7H_7, \text{etc.})$

We find that it is a characteristic feature of every ether-thiourea which we have examined, to react with alcohols, on warming, with transposition of the alkyl groups. In order to purify them by crystallization from an alcohol it is necessary to use, as solvent, an alcohol containing the same alkyl group as that attached to oxygen in the ether-thiourea. Furthermore, the reactions are reversible and are not influenced by the boiling points of the alcohols, or by the size of the alkyl groups involved in the change.

$$R.NHCSNHCH_2OC_2H_5 + CH_3OH \rightleftarrows R.NHCSNHCH_2OCH_3 + C_2H_5OH,$$

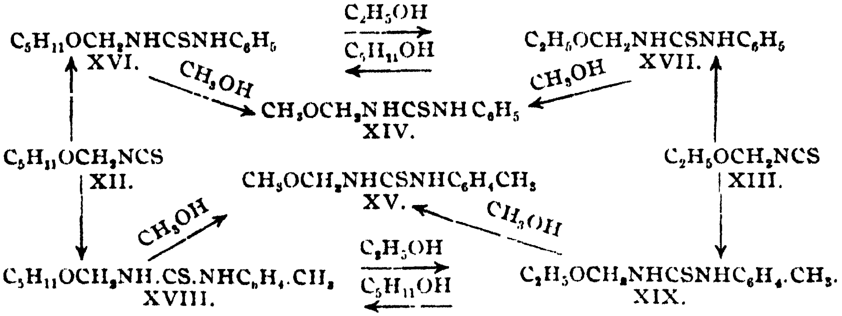
Our experiments were performed with the phenyl and *p*-tolyl ether-thioureas obtained by the action of aniline and *p*-toluidine on isothiocyanomethyl-, -methylethyl and -methylisoamyl ethers.[1] 1-Phenyl-2-isoamoxymethylthiourea (XVI) and 1-phenyl-2-ethoxymethylthiourea (XVII) were both converted smoothly into 1-phenyl-2-methoxymethylthiourea (XIV) by crystallization from methyl alcohol. The structure of this methoxy compound was established by the fact that it was identical with the methoxythiourea obtained by the action of aniline on isothiocyanodimethylether. Crystallization of 1-phenyl-2-isoamoxymethylthiourea (XVI) from ethyl alcohol gave 1-phenyl-2-ethoxymethylthiourea (XVII) which is changed practically quantitatively into the original isoamoxy compound by recrystallization from isoamyl alcohol.

Analogous transformations were obtained with the corresponding *p*-tolyl compounds: 1-Paratolyl-2-methoxymethylthiourea (XV) was prepared by the action of isothiocyanodimethyl ether on *p*-toluidine. This same thiourea was also formed smoothly when 1-paratolyl-2-isoamoxymethylthiourea (XVIII) and 1-paratolyl-2-ethoxymethylthiourea (XIX) were crystallized from methyl alcohol. Crystallization of 1-paratolyl-2-isoamoxymethylthiourea (XVIII) from ethyl alcohol gave 1-paratolyl-

---

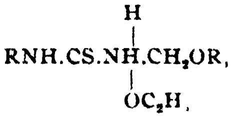
[1] Johnson and Guest, *Loc. cit.*

2-ethoxymethylthiourea (XIX), which is converted smoothly into the original isoamoxy derivative when warmed with isoamyl alcohol. These various transformations are represented by the following formulas:

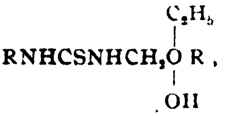


It is therefore possible, by application of this reaction, to prepare a whole series of ether-thioureas, RNH.CSNH.CH$_2$OR′, from one isothiocyanomethylether, R′OCH$_2$.NCS. In case it should be observed that certain primary, aliphatic halogen-ethers do not react, or perhaps react abnormally with potassium thiocyanate giving stable thiocyanates R.SCN, this reaction might be indispensable for the preparation of their corresponding thiourea derivatives.

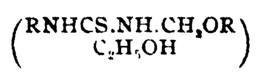
It appears to the writers that the simplest explanation of these characteristic transformations of ether-thioureas is to assume the intermediate formation of unstable addition products, which then break down, giving a new thiourea and alcohol. Whether this involves an addition of the alcohol to nitrogen, as assumed by Decker, giving a compound XX, or an addition to the oxygen atom giving a carboxonium compound XXI, or thirdly a polymolecule XXII, we have at present no knowledge.


$$RNH.CS.\overset{H}{\underset{OC_2H_5}{N}}H.CH_2OR,$$

XX.


$$RNHCSNHCH_2\overset{C_2H_5}{\underset{OH}{O}}R,$$

XXI


$$\left(\begin{matrix}RNHCS.NH.CH_2OR\\ C_2H_5OH\end{matrix}\right)$$

XXII

The results which we have obtained do not support the theory advanced by Gadamer to explain the mechanism of the reaction of a cyclic alcoholate with alcohol. According to this interpretation, when an alcoholate reacts with alcohol, there is first a rupture of the bond between carbon and nitrogen of the alcoholate with intermediate formation of an aldehyde. In the case of an acyclic compound like 1-phenyl-2-ethoxymethylthiourea (XXIII), therefore, according to this explanation, formaldehyde (XXV) and phenylthiourea (XXIV) would be intermediate products of the reaction.

$$\underset{\text{XXIII.}}{C_6H_5NHCSNH.CH_2OR} \xrightarrow{H_2O} \underset{\text{XXIV.}}{C_6H_5NHCSNH_2} + \underset{\text{XXV.}}{CH_2O} + HOR.$$

If a hydrolysis of this character takes place then one would expect to obtain the same ether-thiourea by simply dissolving phenylthiourea in an alcoholic solution of formaldehyde. The facts do not support such a conclusion. We obtained no evidence of the formation of ether-thioureas when phenylthiourea or *p*-tolylthiourea were crystallized repeatedly from a methylalcohol solution of formaldehyde. They separated unaltered, and melting constantly at 154° and 188°, respectively.

III. Experimental Part.

1. Crystallization from Methyl Alcohol: 1-Phenyl-2-methoxymethylthiourea, $C_6H_5NHCSNHCH_2OCH_3$.—This thiourea was formed smoothly by recrystallization of 1-phenyl-2-ethoxymethylthiourea (m. 125–6°) from methyl alcohol. It separated in prismatic crystals melting at 133° (Kjeldahl):

Calculated for $C_9H_{12}ON_2S$: N, 14.28; found, 14.28.

This same thiourea, melting at 133°, was also obtained by crystallizing 1-phenyl-2-isoamoxymethylthiourea (m. 109°) from methyl alcohol (Kjeldahl):

Calculated for $C_9H_{12}ON_2S$: N, 14.28; found, 14.10.

1-Paratolyl-2-methoxymethylthiourea, $CH_3.C_6H_4NHCSNHCH_2OCH_3$, was prepared by crystallizing 1-paratolyl-2-ethoxymethylthiourea (m. 120°) from methyl alcohol. It melted at 129° to a clear oil. The same thiourea was also formed smoothly when 1-paratolyl-2-isoamoxymethylthiourea was crystallized from methyl alcohol (Kjeldahl):

Calculated for $C_{10}H_{14}ON_2S$: N, 13.33; found, 13.42, 13.30.

2. Crystallization from Ethyl Alcohol.—(*a*) When 1-phenyl-2-isoamoxymethylthiourea (m. 109°) was dissolved in hot, absolute ethyl alcohol and the solution cooled, pure 1-phenyl-2-ethoxymethylthiourea separated and melted at 125–6°. A mixture of this thiourea and the thiourea made from aniline and isothiocyanomethylethyl ether melted at the same temperature (Kjeldahl):

Calculated for $C_{10}H_{14}ON_2S$: N, 13.33; found, 13.08.

(*b*) When 1-paratolyl-2-isoamoxymethylthiourea was crystallized from hot, absolute ethyl alcohol it was converted smoothly into 1-phenyl-2-ethoxymethylthiourea melting at 120° to a clear oil (Kjeldahl):

Calculated for $C_{11}H_{16}ON_2S$: N, 12.43; found, 12.40.

3. Crystallization from Isoamyl Alcohol.—(*a*) 1-Phenyl-2-ethoxymethylthiourea (m. 125–6°) was crystallized two times from isoamyl alcohol when it was completely changed to 1-phenyl-2-isoamoxymethylthiourea melting at 109°. A mixture of this thiourea and the thiourea prepared from isothiocyanomethylisoamyl ether and aniline melted at the same temperature (Kjeldahl):

Calculated for $C_{12}H_{20}ON_2S$: N, 11.11; found, 10.99.

(*b*) 1-Paratolyl-2-isoamoxymethylthiourea (m. 119°) was obtained when 1-paratolyl-2-ethoxymethylthiourea was crystallized from isoamyl alcohol (Kjeldahl):

Calculated for $C_{14}H_{22}ON_2S$: N, 10.52; found, 10.56.

NEW HAVEN, CONN.

PHENYL ETHER AND SOME OF ITS DERIVATIVES.

BY ALFRED N. COOK

Received July 12, 1910

Bromination of Phenyl and Tolyl Ethers.

The ethers employed were all prepared by distilling the aluminium salts of the corresponding phenols. While the yield of phenyl and metatolyl ether was good, the yield of the ortho- and paratolyl ether was so small that, in some instances, it was found difficult to obtain a sufficient amount of some of the bromine derivatives to purify sufficiently to yield very satisfactory results on analysis, which accounts for some instances given below where there is considerable difference between the results of analysis and the requirements of calculation. The best yield of phenyl ether was obtained by distilling aluminium phenolate with a sharp heat; but in case of the tolyl ethers, the best yield was obtained by distilling with a low heat. A sharp heat gives rise to a greater proportion of higher boiling substances and less of the ether.

On distilling some aluminium paracresolate with a sharp heat, a peculiar phenomenon was observed, which was not noted in connection with the distillation of any other aluminium salt of the phenols. Bright flashes of light followed one another in quick succession on the surface of the boiling and decomposing liquid. This recalls the fact noted in connection with the distillation of aluminium phenolate in the preparation of phenyl ether, that the escaping gases occasionally ignited spontaneously on coming in contact with the air. In the present case, however, the evolving gases had not yet come in contact with oxygen and the phenomenon could not have been due to combustion.

On distilling some aluminium paracresolate which had been kept for a couple of months in a bottle with a defective cork, through which air had gained access and acted upon the substance, it was found that it yielded paracresol and almost no paratolyl ether and higher boiling substances. It did not melt down as the freshly prepared substance does, even when highly heated. It was found to dissolve very readily in absolute alcohol, carbon disulphide and various other organic solvents. On adding a little water to the solution there was thrown down a voluminous gelatinous precipitate. Its action is therefore exactly analogous to that of aluminium phenolate to which air in limited amount has had access for some time, and which has been described in a previous paper. *An* *investigation into the character and causes of these changes is now in progress in the chemical laboratory of the University of South Dakota.*

Bromination of Phenyl Ether.—Hoffmeister[1] prepared dibromophenyl ether by slowly adding bromine to phenyl ether dissolved in carbon disulphide, kept well cooled until the red color of the bromine ceased to vanish. Melting point, 55°. In an endeavor to prepare a higher bromine derivative, I added a large excess of bromine to some phenyl ether and allowed it to stand for three days with occasional shaking. The carbon disulphide was removed by evaporating on the water bath, which operation also removed a portion of the bromine not acted upon. The remainder of the excess of bromine was removed by washing with caustic soda solution. There was obtained a light yellow liquid of the consistency of glycerol, which failed to solidify on standing three months. It boiled at 240–260° at 30 mm. On analysis it yielded 59.6 per cent. of bromine. Theory would require 65.84 per cent. for the tetrabromo derivative and 48.78 per cent. for the dibromo derivative. It was apparently a mixture of the dibromo and tetrabromo derivatives, 36.5 per cent. of the former and 63.5 per cent. of the latter. From the experiments described below, one would not expect that a higher bromide would be found in the mixture.

Tetrabromophenyl ether ($(C_6H_3Br_2)_2O$) was prepared by gradually adding an excess of bromine to phenyl ether dissolved in carbon disulphide, to which had been added a little iodine to act as a carrier, and shaking meanwhile. The addition of iodine greatly facilitated the reaction, which was clear cut and rapid. In the beginning hydrobromic acid was given off very rapidly but gradually subsided and seemed to cease when sufficient bromine had been added to form the tetra compound. The solution was allowed to stand at room temperature for some time and then heated on the water bath to drive off the carbon disulphide and excess of bromine. There was obtained a red, viscous substance which became milk-white on washing with a solution of caustic soda, and on stirring with cold water it suddenly solidified. The yield of the crude product was quantitative and quite pure It distilled at 280–290° at 25 mm. and at 410–425° under ordinary atmospheric pressure. It is soluble in carbon disulphide and petroleum ether and insoluble in water, alcohol and most organic solvents. It crystallized in large, radial aggregations of swordlike needles The crystals obtained were about three-fourth inch in diameter. On cooling, *per se*, it likewise collects in radial masses on solidification. It is odorless and tasteless and colorless, but on continued exposure to light it turns slightly brownish. It melts at 83–84°. On analysis it yielded 65.56 per cent. of bromine. Calculated for $(C_6H_8Br_2)_2O$, 65.85 per cent.

[1] *Ann.*, **159**, 210.

Attempts were made to prepare the hexabromo, octobromo and decabromo derivatives. A little more than the calculated amount of bromine in each case was allowed to stand in contact with phenyl ether in the presence of iodine for several days with occasional shaking. In every case there was obtained only the tetrabromophenyl ether as shown by the melting point and analysis for bromine.

Dibromometatolyl ether ($CH_3C_6H_2Br—O—BrC_6H_2.CH_3$) was prepared by adding very gradually, with constant shaking, a little more than the theoretical amount of bromine to metatolyl ether dissolved in several times its weight of carbon disulphide. When the calculated amount of bromine required to form the dibromo derivative was added to the substance, *per se*, or in solution in carbon disulphide, in the dark, in direct sunlight, heated to the boiling point, at the temperature of the boiling water bath, at room temperature or at —20°, there was always formed, with equal facility, a dibromo compound which was identical in every instance. The yield was little short of quantitative. It was purified by repeated distillation, discarding the highest and lowest boiling portions each time. A portion was obtained which melted at 48°, but began to soften a few degrees lower. The substance boils at 340–350° (uncor.) under ordinary atmospheric pressure and at about 250° under 15 mm. pressure. The dibromo compound is a white, crystalline solid, which turns yellow with age. It tends to crystallize in warty aggregations on cooling from the molten state. It is soluble in carbon disulphide, alcohol, ether and several other organic solvents; sparingly soluble in absolute methyl alcohol and insoluble in water.

The substance was boiled with water and then with a strong solution of sodium hydroxide in the hope of introducing the hydroxyl group in place of the halogen atom, but without result. It was then heated in a closed tube to 200° for several hours with a strong solution of sodium hydroxide but there was no indication of any reaction. On analysis it yielded 44 55 per cent. of bromine. Calculated for $C_{14}H_{12}OBr_2$, 44 94 per cent.

Tetrabromometatolyl ether ($CH_3C_6H_2Br_2—O—C_6H_2Br_2.CH_3$) was found to be best prepared by adding an excess of the bromine required by calculation directly to the metatolyl ether in the presence of a little iodine and heating on the water wath to drive off the surplus bromine. The yield was very good. The substance was purified by repeated fractional distillation under diminished pressure. It boils at 260–270° under 35 mm. pressure, but decomposes when distilled under ordinary atmospheric pressure.

It is a light yellow, sticky, viscous substance, which crystallizes in warty aggregations on standing for some time. It becomes fluid on gently warming and is sôluble in carbon disulphide, but is insoluble in alcohol, ether, and most common organic solvents. The compound was boiled with water, a strong solution of potassium hydroxide, and water and precipitated calcium carbonate, respectively, for some hours, without any evidence of chemical action. It was heated in a closed tube with each of these reagents for three or four hours, at 200–300°. The tube containing potassium hydroxide showed some signs of chemical action, but it was by no means complete—in fact, it was only in the initial stage. The filtrate yielded a precipitate with silver nitrate in the presence of nitric acid which was soluble in ammonium hydroxide, and a small quantity of an organic substance, presumably, a hydroxymetatolyl ether, was precipitated by neutralizing with an acid. An analysis yielded 61.85 per cent. of bromine. Calculated, 62.26 per cent.

In one experiment in the bromination of metatolyl ether, the bromine was added to the metatolyl ether, *per se*, at 150° in direct sunlight, but the bromine, as shown by various experiments, was as firmly bound as in brominating at 0°. When double the amount of bromine was added, or even a much larger excess, there was produced, with equal readiness, a tetrabromo compound under varying conditions of sunlight and darkness, heat and cold. Some of the tetrabromo compound always appeared to be formed in preparing the dibromo derivative by employing the amounts of reacting substances required by calculation, and there always remained some of the other unacted upon, but only a very small amount. The reaction was quite clear cut and the two foreign substances were readily separated from the dibromometatolyl ether by fractional distillation. In the preparation of the tetrabromo derivative by employing the amounts of the reacting substances required by calculation, there was obtained a little tar and a very little of the dibromo compound was obtained, but the reaction was far more clear cut than is usual in similar cases. It proved impossible to induce metatolyl ether to combine with more than four atoms of bromine, no matter how large an excess was added. No carrier was used in these experiments. Subsequently metatolyl ether was brominated in the presence of a little iodine in order to determine whether a higher derivative would be formed, but only the tetrabromo compound was obtained, nor did the presence of iodine seem to facilitate the reaction to any extent. It would appear, therefore, that metatolyl ether is more easily brominated than phenyl ether.

I believe, for the following reasons, that the bromine enters the nucleus and not the side chain in these experiments. The bromine derivatives effectually resisted all attempts to prepare from them compounds analogous to benzyl alcohol and benzaldehyde by all of the common methods. The bromine is very firmly linked in these compounds, and all attempts to introduce the hydroxyl group in its place were unsuccessful. This is in accordance with what would be expected if the halogen entered the nucleus. Neither of the two compounds, when purified, gave off vapors which attack the mucous membrane of the eyes, as in case of substances formed by the halogen entering the side chain, but when freshly prepared, and before purification, they did have this property, indicating the possible formation of a small quantity of the side chain compounds. Perhaps the halogen might be induced to enter the side chain by employing a still higher temperature, in direct sunlight, but [illegible]riment was not tried on account of lack of both time and ma- [illegible]

[illegible]lyl ethers are markedly different from toluene and its homologs in their action toward bromine, for in these the halogen enters the side chain in direct sunlight, or at the boiling point of toluene, and it enters the nucleus in the dark, when cold.

4-Methyl-2',4'-Dinitrophenyl Ether and Derivatives.

Having carried out a number of reactions between potassium phenolate and the potassium cresolates, which have been reported in this and other journals, it was thought that it might be interesting and profitable to extend the study to bromdinitro benzene.

4-Methyl-2',4'-dinitrophenyl ether ($CH_3C_6H_4OC_6H_3(NO_2)_2$) was prepared by mixing molecular equivalents of potassium paracresolate and 1 bromo-2,4-dinitrobenzene and warming very gently to start the reaction. (In one instance when the two reacting substances had been finely powdered and intimately mixed, the reaction took place at ordinary room temperature, with considerable rise of temperature.) When the action was well started a gentle ebullition took place, which gradually died down when the reaction was completed.

The resulting substance was dissolved in hot alcohol, filtered from the precipitated bromide, and allowed to crystallize. After three recrystallizations it melted sharply at 93°. The yield was nearly quantitative. It is a yellow-colored substance, very soluble in hot alcohol, but sparingly soluble in the cold. It is also quite soluble in various other organic solvents. Analysis for nitrogen yielded 10 64 per cent. Calculated, 10 22 per cent.

On adding a solution of sodium hydroxide to some of the substance a reaction at once set up with evolution of heat. The compound was apparently saponified with the production of paracresol and 2,4-dinitrophenol.

The free sulphonic acid ($(NO_2)_2C_6H_3OC_6H_3CH_3SO_3H$) was prepared by dissolving the ether in concentrated sulphuric acid, by the aid of the boiling water bath, precipitating the excess of sulphuric acid with freshly prepared lead chloride, and then precipitating the lead with hydrogen sulphide and evaporating to crystallization.

It is very soluble in water and shows a tendency to crystallize in radial aggregations of fine needles, like many other derivatives of phenyl ether.

On heating to 85° in the air bath in contact with air it melted and lost in weight corresponding to one and one-half molecules of water of crystallization. However, when heated in a melting-point tube, it did not melt until the temperature of 150° was reached and then with apparent decomposition. When a weak water solution was mixed with sodium carbonate, calcium carbonate, and barium carbonate, it caused a brisk evolution of carbon dioxide. Its water solution is only slightly yellow but a solution of the barium salt in water is quite yellow, which becomes much more intense on heating. A solution of the sodium salt is much yellower still and intensifies on warming a few degrees.

Analyses resulted as follows:

Calculated for $C_{13}H_{10}O_8S + 1^1/_2H_2O$: S, 8.4 ; H_2O, 9 61
Found: S, 8 28; H_2O, 9 69, 9 53.

The barium salt, $((NO_2)_2C_6H_3OC_6H_3CH_3SO_3)_2Ba$, was prepared by dissolving the ether in concentrated sulphuric acid and diluting with a large amount of water, treating with an excess of barium carbonate to precipitate the sulphuric acid and change the sulphonic acid to the barium salt and evaporating to crystallization. Attempts to prepare the barium salt as in case of the mononitrophenyl ether, by precipitating the excess of sulphuric acid with barium chloride and then adding a sufficient amount to change the sulphonic acid to the barium salt, were unsuccessful. In attempting to crystallize the product formed, it seemed to decompose and form a compound insoluble in water.

The barium salt is light yellow in color, but when heated to 100° it assumes a much deeper tint. The water solution is much yellower than the salt itself. It is different from most of the barium salts of the sulphonic acid derivatives of the phenyl ethers thus far prepared in that it does not contain any water of crystallization.

On adding a few drops of concentrated hydrochloric acid to a solution of the barium salt, it clears up immediately, probably due to the formation of barium chloride and the liberation of the free sulphonic acid, which is nearly colorless. Two analyses yielded 16.30 and 16.29 per cent. of barium; calculated for $(CH_3.(NO_2)_2.C_7H_6OSO_3)Ba$, 16.34 per cent.

The sodium salt $((NO_2).C_6H_3OC_8H_8.CH_3SO_3NO)$ was prepared by precipitating the barium of the barium salt with sodium carbonate and also by neutralizing the free sulphonic acid with sodium carbonate and evaporating to crystallization in each case. When dry, the salt is light yellow in color but when moist it is brilliant yellow. Its water solution is very yellow. On adding a few drops of strong acid to a solution in water, the yellow color almost entirely disappears. It melted at 145°. On heating to 100°, it loses in weight, corresponding to one and one-half molecules of water of crystallization. On coming in contact with the air again for a few hours, it absorbs moisture from the air until it attains its original weight. An analysis resulted as follows:

Calculated for $C_{13}H_9O_8N_2SNa + 1^1/_2H_2O$: Na, 6 00; H_2O, 2.29.
Found: Na, 6.11; H_2O, 2.55.

Other Salts.--Attempts were made to prepare the chromium and cobalt salts by precipitating the barium from the barium salt by means of chromium sulphate and cobalt sulphate. Substances were obtained which were supposed to be the salts sought but they both decomposed on attempting to purify them by crystallization.

2 : 4-Dinitro-p-phenoxybenzoic acid ($(NO_2)_2.C_6H_3OC_6H_4.COOH$) was prepared by dissolving the dinitrophenylmethyl ether in glacial acetic acid and, while warming on the water bath, adding a solution of chromic anhydride in water until a test portion would yield a precipitate on addition of a large volume of water which would completely dissolve on addition of an alkali.

The acid was purified by dissolving in a dilute solution of ammonia, boiling off the excess of ammonia, precipitating the free acid again by adding hydrochloric acid and washing the precipitate free from chlorine. The acid is of a canary-yellow color. It is insoluble in water, ether, petroleum ether, methyl alcohol and benzene. It is only slightly soluble in ethyl alcohol It did not melt when heated to 200°.

The silver salt ($(NO_2)_2.C_6H_3OC_6H_4.COOAg$) was prepared by precipitation by adding silver nitrate to a solution of the ammonium salt obtained as described above. It is of a canary-yellow color at ordinary temperature, but darkens when heated to 100°, but does not lose in weight. Analysis yielded 26 09 per cent. of silver. Calculated, 26 27 per cent

Only one other of the nitrophenyl ethers heretofore prepared has yielded a carboxylic acid by oxidizing the side chain with chromic acid in acetic acid solution.

2,4-Dinitrophenyl Ether and Derivatives.

(The experimental work of this chapter was carried out by Mr. Carl Englund, under my direction.)

2,4-Dinitrophenyl ether ($C_6H_5OC_6H_3(NO_2)_2$) was prepared by grinding up in a mortar equimolecular quantities of potassium phenolate and 1,2,4-bromodinitrobenzene. A reaction began in the cold which was carried to completion by heating on a water bath. There resulted dinitrophenyl ether in the form of a brown oil and solid potassium bromide. The oil distilled without decomposition at 230–250° under a pressure of 27 mm. and solidified after standing for a short time. It was crystallized from hot alcohol several times and then melted sharply at 70°. The yield was quantitative.

2,4-Dinitrophenyl ether is very soluble in alcohol and various other organic solvents and slightly soluble in water. It has a faint odor and a burning, biting taste. An analysis for nitrogen yielded the following results: Calculated for $C_{12}H_8O_5N_2$, 10.70 per cent; found, 10.75 per cent.

Attempts to reduce the nitro groups with tin and hydrochloric acid were unsuccessful. The base decomposed immediately on exposure to the air.

Some of the 2,4-dinitrophenyl ether was heated with water at 100° for several hours in closed tubes with the idea of hydrolyzing the substance, but without effect. However, when heated under the same conditions with sodium hydroxide, chemical reaction had taken place. The tube was filled with ammonia gas and crystals of a foreign substance were deposited on standing. On account of lack of time, however, they were not studied farther.

2,4-Dinitrophenylethersulphonic acid ($(NO_2)_2.C_6H_3OC_6H_4.SO_3H$) was prepared by gently warming 2,4-dinitrophenyl ether with concentrated sulphuric acid. It yielded a solution which was not precipitated by the addition of water. The excess of sulphuric acid was precipitated by the addition of barium chloride On evaporating the filtrate on the water bath, the sulphonic acid was obtained in the form of pearly white flakes. It is easily soluble in water and has a strong, bitter taste much like picric acid.

The analysis for sulphur (though now lost) yielded results which corresponded with the requirements of theory.

The barium salt ($((NO_2)_2C_6H_3OC_6H_4.SO_3)_2Ba + {}^1/_2H_2O$) of the sulphonic acid was obtained by adding an excess of barium chloride to the solution of the sulphonic acid in dilute sulphuric acid, obtained as described above. On evaporating over the water bath, the barium salt of the sulphonic acid was obtained in the form of pearly flakes which do not melt without decomposition. It is difficultly soluble in cold water but readily soluble in hot water. On heating in the air bath to 200°, it lost in weight corresponding to one-half molecule of water of crystallization. Two analyses for barium yielded 16.93 per cent. and 16 86 per cent., respectively. Required by calculation, 16.85 per cent.

Several unsuccessful attempts were made to prepare other salts. Strontium carbonate, copper carbonate, and potassium carbonate were added to solutions of the pure sulphonic acid, and although effervescence took place in each case, no well defined salts were isolated.

Trinitrophenyl ether, $C_{12}H_7O(NO_2)_3$, was obtained by dissolving the dinitrophenyl ether in strong nitric acid. On pouring this mixture into water, there was precipitated a gummy mass, which solidified on rubbing up with cold water. It was crystallized from methyl alcohol and obtained in the form of warty masses and radiating clusters of yellow prismatic crystals. Two analyses yielded 14.29 and 14.23 per cent., respectively, of nitrogen. Calculation requires 13.77 per cent.

Bibliography.

(1) *Ann.*, **90**, 209.—List and Limpricht obtained diphenyl ether as one of the products of the destructive distillation of copper benzoate. (2) *Ann.*, **125**, 328.—Rudolph Fittig obtained diphenyl from the above-mentioned distillate. (3) *Ann.* **138**, 375.—C. Lesimple obtained a compound by distilling phenyl phosphate with lime, which he called phenyl ether. (4) *Ann.*, **159**, 191, and *Ber.*, **3**, 747.—W. Hoffmeister prepared phenyl ether by treating diazobenzene sulphate with phenol and made a thorough study of the compound. (5) *Ber.*, **23**, 3709.—Hirsch varied Hoffmeister's method and greatly increased the yield. (6) *Ber.*, **6**, 564.—Maikopar made a dinitro derivative by acting on dinitrochlorobenzene with an alcoholic solution of potassium hydroxide and phenol. (7) *Ber.*, **12**, 762.—Willgerodt prepared a dinitrophenyl ether by the above method. (8) *Ber.*, **12**, 1277.—Willgerodt prepared a trinitrophenyl ether by the same method. (9) *Ber.*, **13**, 887.—Willgerodt prepared a tetranitro derivative by heating dinitropotassium phenolate with dinitrochlorobenzene in a sealed tube. (10) *Ber.*, **14**, 187.—Merz and Weith prepared phenyl ether by heating phenol with zinc chloride, and also aluminium chloride (see also correspondence, *Ber.* **12**, 1925). (11) *Ber.*, **15**, 1123.—Niederhausern prepared methylene diphenyl oxide by distilling sodium phenolate with sodium metaphosphate. (12) *Ber.*, **17**, 1764.—Willgerodt and Huetlin prepared derivatives by acting on potassium phenolates with dinitrochlorobenzene and picryl chloride. (13) *Ber.*, **17**, 2638.—Bausch prepared a dimethyl derivative by heating paracresol with zinc chloride. (14) *Ber.*, **29**, 1446.—Haeussermann and Teichman prepared various derivatives by acting on halogen nitrobenzene derivatives with potassium or sodium phenolates. (15) *Ber.*, **29**, 1878.—F. Ullman, independently, from the above-mentioned investigators, made a few compounds by the same method. (16) *Ber*, **29**, 2083, and *Ibid*, **30**, 738.—Haeussermann and Bauer continued the work begun by Haeussermann and Teichman and prepared numerous compounds. (17) *J. Chem. Soc.*, **41**, 5, and *Ibid*, **49**, 27.—Gladstone and Tribe prepared phenyl ether and derivatives by distilling aluminium phenolate, aluminium thymolate, and aluminium cresolates. (18) *Chem. News*, **42**, 3.—See No. 15 above. (19) *Chem. News*, **42**, 146.—See No 8 above. (20) *J. prakt. Chem.*, **1**, 143.—See No. 4 above. (21) *J. prakt. Chem*, (2) **28**, 273.—Klepl prepared carbonyl phenyl oxide by the action of triphenyl phosphate on sodium salicylate. (22) *J. prakt. Chem*, (2 **28**, 193.—Klepl prepared phenyl ether by distilling paraphenoxybenzoic acid with caustic baryta. (23) *J. prakt. Chem.*, (2) **28**, 201.—Richter prepared diphenyl oxide by distilling sodium salicylate and triphenyl phosphate. (24) *Monatshefte*, **17**, 65.—B. Jeitles distilled calcium phenyl phosphate and obtained, among other things, diphenyl ether. (25) *Gazetta*, **28**, (1) 197.—G. Ortoleva and A. Paratoner treated diphenyl ether with sulphonyl chloride and obtained chlorine derivatives. (Abstract in *J. Chem. Soc.*, 1898.) (26) *Am. Chem. J.*, **24**, 525.—Cook and Hillyer prepared 2-nitro-4′-methylphenyl ether and several derivatives. (27) THIS JOURNAL, **23**, 806.—Cook prepared 2-nitro-2′-methylphenyl ether and several derivatives. (28) THIS JOURNAL, **24**, 1200.—Cook and Eberly prepared 4-nitro-2′-methylphenyl ether and various derivatives. (29) *Am. Chem. J.*, **28**, 486.—Cook and Frary prepared 4-nitro-3′-methylphenyl ether and various derivatives. (30) THIS JOURNAL, **25**, 60.—Cook prepared 4-nitro-4′-methylphenyl ether and various derivatives. (31) THIS JOURNAL, **26**, 302.—Cook described the properties of phenyl ether. (32) Proceedings of the Iowa Academy of Sciences, **10**, 116.—Cook made a study of the Hirsch-Hoffmeister method of preparing phenyl ether. (33) *Ber.*, **37**, 853.—Ullman prepared phenoxybenzoic acid by heating orthochlorobenzoic acid with potassium phenolate in the presence of copper. (34) *Ber.*, **32**, 2211.—Ullman and Sponagle prepared phenyl ether by the above-mentioned method. (35) *Ann.*, **350**, 83.—Ullman and

Sponagle prepared various methylphenyl ethers, using copper as a catalytic agent. (36) This Journal, 28, 608.—Cook studied aluminium phenolate with reference to the preparation of phenyl ether. (37) *Ber.*, 38, 2490.—Kipper prepared several derivatives of phenyl ether by means of Friedel and Crafts' reaction. (38) *Am. Chem. J.*, 36, 543.—Cook prepared metatolyl ether and several of its derivatives

State University, Vermilion, S. Dak.

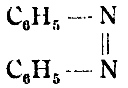
THE STEREOMERIC AZOBENZENES.

By Catherine V. Gortner and Ross Aiken Gortner

Received June 10, 1910.

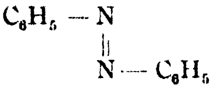
Introduction.

It is apparent from the structural formula of azobenzene that two stereomeric modifications should exist, one in which both aromatic nuclei are on the same side of the nitrogen bridge or *syn*-azobenzene (I), and the other where the nuclei are opposite each other or *anti*-azobenzene (II):



$$\begin{array}{r}C_6H_5-N\\ \|\\ C_6H_5-N\end{array}$$

(I)



$$\begin{array}{l}C_6H_5-N\\ \qquad\quad\|\\ \qquad\quad N-C_6H_5\end{array}$$

(II)

Although many such examples of syn and anti forms are known in the diazo compounds,[1] the authors are not aware of any such isomerism having been observed in the azo group.

Some years ago one of us had occasion to prepare azobenzene during a course in "organic preparations," but could not by any means obtain a compound melting at 68°, the melting point of azobenzene as described in the literature. Crystals were, however, obtained which melted at "about 23°," as the notes were then recorded. It afterward seemed probable that this was the unknown stereomeric form and we have recently taken up the subject again, obtaining results which lead us to believe that such was the case.

Experimental.

The azobenzene was produced by the dry distillation of azoxybenzene and clean iron filings from a small non-tubulated retort. The azoxybenzene was prepared according to the method of Lachman.[2]

Thirty grams of nitrobenzene were added to 250 cc. of methyl alcohol containing 40 grams of sodium hydroxide and the mixture heated during three hours on an actively boiling water bath. The methyl alcohol was then distilled off and the residue poured into ice-water. The azoxybenzene separated as an oil which soon became solid. This solid was well washed, melted with dilute hydrochloric acid to remove traces of aniline, washed free of acid, and recrystallized from 90 per cent. alcohol. Prepared in this manner, azoxybenzene forms small straw-colored needles, which melt at 36° (cor.); yield, 15–18 grams.

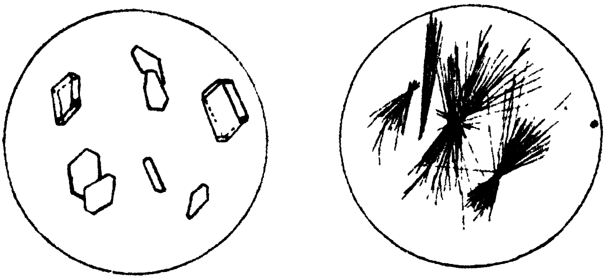
---

[1] Holleman, "Lehrb. d. Organ. Chem.," Leipzig, 1908, p. 362.

[2] This Journal, 24, 1178 (1902).

The azoxybenzene was dried on a porous plate and lastly at 110° for four hours. It was then finely pulverized and mixed with twice its weight of clean, dry iron filings and the mixture distilled. The distillate, in every case, was a red liquid containing a crystalline substance. The red portion was easily soluble in ligroin, leaving a mass of light gray needles, insoluble in ligroin, soluble to a considerable extent in alcohol and ether, containing nitrogen and melting at 237° (cor.), yield, about 1 per cent. of the azoxybenzene taken. This substance was not further investigated.

The deep red ligroin solution was thoroughly washed with cold dilute hydrochloric acid and then with water, filtered, and allowed to evaporate. In a number of instances preparations of azoxybenzene were obtained which yielded only ordinary azobenzene (m. p. 68°) crystallizing in prisms (see fig.). In several cases, however, only a deep red liquid was obtained, which, for a long time, we despaired of obtaining pure, as with the small amount available, distillations always resulted in considerable decomposition. This same red liquid was, also, often found in the mother liquors from which the 68° compound had crystallized.[1] At last, however, crystals were noticed in one preparation, from which other preparations were easily seeded. The crystals so obtained were pressed out on a porous plate, dissolved in ether, and the ether allowed



m.P. 68°   m.P. 25°

Crystals of Azobenzene

---

[1] Gattermann ("Practical Methods of Organic Chemistry," New York, 1903, p. 200) states that "if, on heating, a sudden but harmless explosion should occur, it is due to the fact that the substances were not dry; the experiment should be repeated." The authors have found that if the distillation is continued *after the explosion* a small yield of the "red liquid" usually results which can be easily separated from the "tar" by solution in ligroin. In several instances we have obtained fair yields of 25° azobenzene in this manner, but in no instance have we obtained the 68° modifications from the explosion residue.

to evaporate, the crystals again pressed out on a porous plate and the process repeated until the melting point remained constant. For analysis the product was dried *in vacuo* over concentrated sulphuric acid:

0.1171 gram gave 15.2 cc. nitrogen at 16.5° and 772 mm. Calculated for $C_{12}H_{10}N_2$: N, 15.38 per cent.; Found: N, 15.35 per cent.

This variety of azobenzene forms orange-red, stellate groups of needles (see fig.), is easily soluble in ether, ligroin, alcohol, acetone, methyl alcohol, etc., and melts at 25° (cor.) to a deep red liquid. It will not crystallize when "seeded" with the 68° substance, but in two instances we have succeeded in quantitatively transforming the 25° substance into the 68° substance, once by boiling with dilute hydrochloric acid, and in the other instance the cause of conversion is unknown to us. We can give no method which will always insure conversion, nor have we been able to transform the 68° substance into the 25° modification. According to Holleman,[1] the *syn* modifications are the least stable, so it seems probable that the new compound is *syn*-azobenzene. When a mixture of the two compounds occurs, the 68° isomer easily crystallizes out, leaving the 25° azobenzene practically free of the higher melting substance.

Reduction of the 25° Azobenzene.—1.75 grams of azobenzene melting at 25° were dissolved in 60 cc. of 50 per cent. alcohol and an excess of sodium amalgam was added. The reaction was allowed to proceed in the cold until all color had been discharged. The hydrazobenzene was precipitated from this solution by dilution, filtered off, and washed with dilute alcohol and then with water, dried at 100°, and recrystallized from ligroin, yield 1.50 grams, or 83 per cent. of the theoretical yield, m. p. 126° (cor.). When this hydrazobenzene was allowed to oxidize in the air, in the presence of alkali, and the oxidation mixture extracted with ether, only the 68° azobenzene was found to be present.

Summary.

1. A second stereomeric azobenzene has been isolated.

2. The new modification differs from the 68° isomer by melting at 25° (cor.) and crystallizing in stellate groups of needles.

3. From a mixture of the two isomers the 68° compound may be easily separated by crystallization, leaving the 25° isomer in the mother liquor.

4. The 25° azobenzene (probably *syn*-azobenzene) has been converted into the 68° isomer, but the reverse change has not been accomplished.

COLD SPRING HARBOR, LONG ISLAND, N. Y.

---

[1] Holleman, *Loc. cit.*

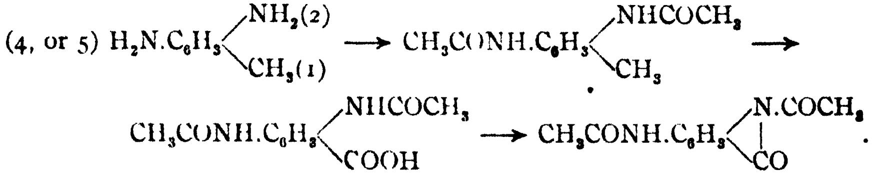
[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 179.]

RESEARCHES ON QUINAZOLINES (TWENTY-FIFTH PAPER). THE SYNTHESIS OF 6- AND 7-AMINO-2-METHYL-4-QUINAZOLONES FROM 4- AND 5-ACETAMINOACETANTHRANILS.[1]

BY MARSTON TAYLOR BOGERT, CARL GUSTAVE AMEND AND VICTOR JOHN CHAMBERS.

Received August 10, 1910.

The 4- and 5-acetaminoacetanthranils were prepared from the corresponding diaminotoluenes by acetylating, oxidizing the acetyl derivatives with potassium permanganate in neutral solution, and treating the diacetamino acids with excess of acetic anhydride:

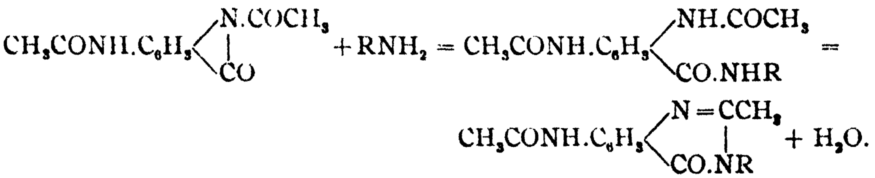


$$(4,\text{ or } 5)\ H_2N.C_6H_3\Big\langle\begin{matrix}NH_2(2)\\ CH_3(1)\end{matrix} \longrightarrow CH_3CONH.C_6H_3\Big\langle\begin{matrix}NHCOCH_3\\ CH_3\end{matrix} \longrightarrow$$

$$CH_3CONH.C_6H_3\Big\langle\begin{matrix}NHCOCH_3\\ COOH\end{matrix} \longrightarrow CH_3CONH.C_6H_3\Big\langle\begin{matrix}N.COCH_3\\ |\\ CO\end{matrix}.$$

The oxidation of the 2,5-diacetaminotoluene proved much more troublesome than that of the 2,4-isomer, and the yield of diacetamino acid considerably less.

By condensing these anthranils with primary amines,[2] acetamino-4-quinazolones result:



$$CH_3CONH.C_6H_3\Big\langle\begin{matrix}N.COCH_3\\ |\\ CO\end{matrix} + RNH_2 = CH_3CONH.C_6H_3\Big\langle\begin{matrix}NH.COCH_3\\ CO.NHR\end{matrix} =$$

$$CH_3CONH.C_6H_3\Big\langle\begin{matrix}N=CCH_3\\ |\\ CO.NR\end{matrix} + H_2O.$$

On splitting off the acetyl group, the free 6- or 7-aminoquinazolones were obtained, from which in turn other derivatives were produced.

The amines used in the experiments were ammonia, methyl, ethyl, normal propyl, secondary butyl and isoamyl amines, aniline, *p*-anisidine, *p*-phenetidine, *p*-aminobenzonitrile, α-naphthylamine, hydrazine, phenylhydrazine, and 7-amino-2-methyl-4-quinazolone. Of these, the condensation with the secondary butylamine (2-aminobutane), for some unknown reason, stopped at the amide stage. The other amines all gave quinazolones.

Of the four possible Bz-monaminoquinazolines, the 5-amino derivatives have been described by Bogert and Chambers[3] and the 7-amino by Bogert and Klaber[1] and Bogert and Kropff.[2] Zacharias[3] prepared a crude 8-amino-2-methyl-4-quinazolone, by reduction of the corresponding nitro compound, but failed to get the substance pure.

---

[1] Read at the meeting of the New York Section, Jan. 7, 1910.

[2] Anschütz, Schmidt and Greiffenberg, *Ber.*, 35, 3480 (1902); Bogert, *et al.*, THIS JOURNAL, 27, 649, 1305, 1327; 28, 94, 884, 1449; 29, 82, 517, 729; etc.

[3] THIS JOURNAL, 28, 208 (1906).

The 6-amino derivatives described in the following pages are the first definitely shown to belong to this series. It seems likely that the aminoquinazolines prepared by Griess[4] and by Niementowski[5] carry the amino group at position 6, although this remains to be proven. The same is true of the diaminoquinazoline of Niementowski,[6] where it is quite probable that the two amino groups are located at 6 and 8, although their position likewise has yet to be determined.

On account of the greater expense of the 2,5-diaminotoluene, most of our experiments were carried out with the 2,4-isomer, and the majority of the products are therefore 7-aminoquinazolines.

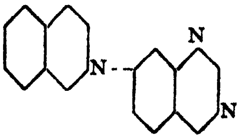
Practically all of the new products are crystalline solids of high melting or decomposing points. Some of the quinazolines are soluble in boiling water. Most of them are more or less soluble in alcohol and insoluble or difficultly soluble in ether. Those carrying the —CO.NH— $\rightleftarrows$ —C(OH) : N— grouping dissolve in cold caustic alkalies and are reprecipitated from these solutions on saturation with carbon dioxide, but this grouping is not affected by acylating agents or by phenylhydrazine.

With chloroform and alcoholic caustic alkali, both 6- and 7-aminoquinazolones give off a faint not unpleasant odor when heated.

By the diazo reaction, the amino group can be replaced by other groups or, by diazotizing and combining with suitable couplers, azo dyestuffs may be produced.

The acetaminoquinazolones can be directly nitrated or brominated.

In former papers from this laboratory[7] we have shown that by condensing acylanthranils with hydrazine hydrate, or with 3-aminoquinazolones, 3,3'-diquinazolonyls may be obtained. We have now found that Bz-amino-4-quinazolones can be similarly condensed with acylanthranils, and in this way have obtained a 3,7'-diquinazolonyl, where the union of the two heterocycles is an N–C instead of an N–N one:



---

[1] This Journal, 30, 810 (1908).

[2] *Ibid.*, 31, 1071 (1909).

[3] *J. prakt. Chem.*, (2) 43, 443 (1891).

[4] *Ber.*, 2, 416 (1869).

[5] *J. prakt. Chem.*, (2) 51, 513 (1895).

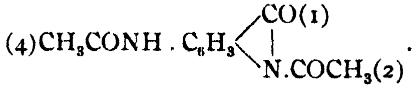
[6] *Loc. cit.*

[7] Bogert and Seil, This Journal, 28, 884, *et al.*

In our study of the properties of 2-methyl-7-acetamino-3-amino-4-quinazolone, we were rather surprised to find that it failed to give the Bülow condensation[1] with diacetosuccinic ester.

Experimental.

I. Preparation of Anthranils.

4-Acetaminoacetanthranil,  $(4)CH_3CONH\,.\,C_6H_3\left\langle\begin{array}{l}CO(1)\\ |\\ N.COCH_3(2)\end{array}\right.$. — The 2,4-diaminotoluene was changed to the diacetaminotoluene by the action of acetic anhydride. The following was found to be the most rapid and satisfactory method of carrying out the acetylation:

Ten g. of the dry and finely pulverized diamine are added at once to about 20–25 g. pure acetic anhydride. An energetic reaction ensues, with considerable rise of temperature. As the reaction abates in violence, the rapidly thickening mass is stirred vigorously to insure complete contact with the anhydride. On cooling, the mass solidifies. The entire reaction is completed in a few minutes and without external heating. The product is washed thoroughly with water and then crystallized from the same, giving long, snowy, silky needles of the pure diacetaminotoluene.[2] From 30 g. pure diamine, we obtained 37.5–38.4 g. of the pure diacetyl derivative.

For most of our work, however, we used a crude commercial toluylenediamine, giving an acetylated product of darker color and in poorer yield. It was found unnecessary to purify this crude acetyl derivative, as the impurities were eliminated in the subsequent oxidation of the compound, and affected only the yield and not the purity of the oxidation product.

The 2,4-diacetaminotoluene was oxidized to the 2,4-diacetaminobenzoic acid by the action of potassium permanganate in neutral solution.[3] On the completion of the oxidation and concentration of the resulting solution of potassium diacetaminobenzoate, some unchanged diacetaminotoluene first separates and should be removed. On acidifying the filtrate, the acid precipitates in microcrystalline condition, sufficiently pure for the preparation of the acetanthranil. Starting with 20 g. of pure diacetaminotoluene, the yield of acid varied from 17.6–19.9 g. and half a gram of diacetaminotoluene was recovered unoxidized. With a like amount of the crude diacetaminotoluene, 2–3 g. remained unoxidized, and 15–16 g. of the acid were obtained.

In an attempt to nitrate this diacetaminobenzoic acid, it was treated with excess of fuming nitric acid at 35°. Most of the diacetamino acid dissolved, and on diluting the solution with water reprecipitated apparently unchanged, for when washed with water and recrystallized from alcohol, fine, colorless needles resulted, of approximately the same melting point (261° cor.) and composition (found: N, 12.0; theory, 11.86) as the original acid.

---

[1] *Ber.*, 39, 2621, 3372 (1907), *et al.*

[2] Koch, *Ann.*, 153, 132.

[3] Ullmann and Uzbachian, *Ber.*, 36, 1803 (1903).

Twenty to twenty-five g. acetic anhydride were heated to gentle boiling and 10 g. well-dried and finely pulverized diacetamino acid slowly stirred in, so that the solution remained fairly clear and gentle boiling continued. In this way, bumping is avoided. When the acid had all been added, the solution was concentrated to about half its original volume, and on cooling the mass solidified in rosettes of pale yellowish or colorless needles of the anthranil. Yield, somewhat over eight grams. Purified by crystallization from acetic anhydride, it forms colorless needles, m. p. 220° (cor.).

Found: N, 13.04. Calculated for $C_{11}H_{10}O_3N_2$: N, 12.90.

It is slightly tribo-electric. In presence of moisture, it is hydrated to the diacetamino acid. Heated with primary amines, it yields 7-acetamino-2-methyl-4-quinazolones.

2,5-Diacetaminobenzoic Acid, $(2,5)(CH_3CONH)_2C_6H_3.COOH$.—2,5-Diacetaminotoluene[1] was prepared by adding the diaminotoluene hydrochloride to a solution of fused sodium acetate in acetic anhydride, the temperature of the solution being maintained above the boiling point of acetic acid, then boiling the solution for a few minutes. When cold, the mixture was diluted with water and the precipitated acetyl derivative recrystallized from water, in which it is much more soluble than the 2,4-isomer. Yield, 21 g. acetyl derivative from 30 g. of the diamine hydrochloride.

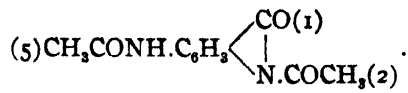
This acetyl derivative was oxidized with potassium permanganate in presence of magnesium sulphate. It is much more difficult to oxidize than the 2,4-isomer. From 10 g. of the diacetaminotoluene and 30 g. potassium permanganate (double the calculated amount), but 4 g. of the acid were obtained. A further increase in the amount of permanganate failed to increase the yield of acid. The acid precipitates usually in an amorphous state, but assumes a crystalline condition on standing. Treated with bone-black and recrystallized from alcohol, it forms minute, colorless crystals, melting with decomposition at 262° (cor.).

Found: N, 11.97. Calculated for $C_{11}H_{12}O_4N_2$: N, 11.86.

It is soluble in strong mineral acids and in aqueous solutions of caustic or carbonated alkalies, but is insoluble in dilute hydrochloric or in acetic acid. It dissolves also in nitrobenzene, aniline, or alcohol, but is not appreciably soluble in ether, carbon tetrachloride, ligroin or benzene.

---

[1] Nietzki, *Ber.*, 10, 1157 (1877); 12, 2237 (1879).



$$(5)\mathrm{CH_3CONH.C_6H_3}\left\langle\begin{array}{l}\mathrm{CO}(1)\\ |\\ \mathrm{N.COCH_3}(2)\end{array}\right.$$

5-Acetaminoacetanthranil, $(5)CH_3CONH.C_6H_3\langle CO(1) | N.COCH_3(2)\rangle$. — Five grams of the diacetamino acid were added to 10 g. hot acetic anhydride and the solution boiled down to one-third its original bulk. On cooling, the anthranil separated in coarse, yellowish-brown needles, which, recrystallized twice from acetic anhydride, still retained a faint yellowish-brown cast and melted at 253° (cor.). Yield, 3.5 g. anthranil from 5 g. acid.

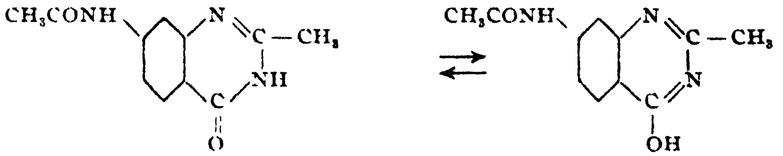
Found: N, 13.02. Calculated for $C_{11}H_{10}O_3N_2$: N, 12.90.

Like its isomer, this anthranil readily takes up moisture and reverts to the diacetamino acid. With primary amines, it yields 6-acetamino-2-methyl-4-quinazolones.

II. Quinazolones from 4-Acetaminoacetanthranil.

With the exception of the first compound, all the following quinazolines carrying the —CO.NH— $\rightleftarrows$ —C(OH) : N— group are, for the sake of brevity, denominated quinazolones and given the —CO.NH— formula.

7-Acetamino-2-methyl-4-quinazolone (*7-Acetamino-2-methyl-4-hydroxyquinazoline*),



Eight g 4-acetaminoacetanthranil were added to 50 cc. dilute ammonium hydroxide solution (10 cc. ammonium hydroxide solution of sp. gr. 0.9 to 40 cc. water) and the mixture heated a few minutes. The thick paste resulting was diluted with water to about 400 cc. and boiled for several minutes. Part dissolved and part separated (with more ammonia, a clear solution can be obtained, but the excess of ammonia must then be boiled off, or the separation of the product is not so complete). On cooling, the quinazolone separated form the solution in fine, short, silky, colorless needles, softening in the neighborhood of 342° and melting at 344° (cor.). Yield, 5.5 g.

Found: N, 19.53. Calculated for $C_{11}H_{11}O_2N_3$: N: H_2O, 19.35.

It is easily soluble in boiling water or in alcohol, slightly soluble in ethyl acetate, very difficultly soluble or insoluble in ether, carbon tetrachloride or toluene.

From water it crystallizes with water of crystallization: 1.0363 g. air-dried sample lost 0.15 g. on drying to constant weight at 100–10°.

Found: H_2O, 14.46. Calculated for $C_{11}H_{11}O_2N_3.2H_2O$: H_2O, 14.23.

7-Amino-2-methyl-4-quinazolone.—Five and one-half g. of the above acetyl derivative were boiled for about an hour with dilute potassium hydroxide solution (5 g. KOH to 50 cc. water), the solution cooled, diluted, filtered, and the filtrate saturated with carbon dioxide. The aminoquinazolone separated in fine, silky, colorless hairs, rapidly assuming a faint pinkish cast on standing. It can be further purified by recrystallization from dilute alcohol. From water it crystallizes with half a molecule of water of crystallization:

Found: H_2O, 4.8. Calculated for $(C_9H_9ON_3)_2\ H_2O$: H_2O, 4.9.

The anhydrous compound melts at 311° (cor.).

Found: C, 61.7 and 61.8; H, 5.1 and 5.2. Calculated for $C_9H_9ON_3$: C, 61.7; H, 5 1.

The substance is therefore identical with the 7-amino-2-methyl-4-quinazolone prepared by Bogert and Klaber[1] by reduction of the corresponding nitro compound.

It is tribo-electric, and gradually darkens on standing in the air. It is readily soluble in hot acetone, very slightly soluble in hot benzene, and apparently insoluble in ligroin. Boiled with alcoholic potassium hydroxide solution and chloroform, it emits an odor, presumably of an isonitrile, and yet of a rather pleasant banana-like character.

Bogert and Seil[2] found that when 5-nitro-2-methyl-3-amino-4-quinazolone was heated with phenylhydrazine, the 3-amino group was replaced by the phenylhydrazino group and the CO of the quinazolone reacted with a second molecule of the hydrazine, the result being a phenylhydrazinophenylhydrazone. A similar reaction did not occur when the above 7-amino-2-methyl-4-quinazolone and phenylhydrazine were heated together, alone or in alcoholic solution. No ammonia was evolved and the original quinazolone was recovered unaltered. It seems strange that the Bz-amino group failed to react, as an aromatic amino group can thus often be replaced directly by the phenylhydrazino group.

When the aminoquinazolone was boiled with formaldehyde and potassium cyanide, a reaction took place, but we failed to isolate any new products from the mixture. No change occurred when the aminoquinazolone was boiled with ethyl chloroacetate.

Azo dyestuffs can readily be produced from this amine by the usual diazotizing and coupling reactions.

Potassium Salt.—Square, colorless plates, easily soluble in cold water, but slightly soluble in alcohol.

Hydrochloride.— Prepared by the action of strong hydrochloric acid upon the free base or upon its ethyl acetate solution. Light brown, granular powder, decomposing on heating.

Chloroplatinate—Red, granular crystals.

Found: Pt, 25.6. Calculated for $(C_9H_{10}ON_3)_2PtCl_6$: Pt, 25.6.

---

[1] THIS JOURNAL, 30, 810 (1908).

[2] *Ibid.*, 28, 88 (1906).

Dinitro-7-acetamino-2-methyl-4-quinazolone. — The acetaminoquinazolone was added to a slight excess of fuming nitric acid at room temperature. It dissolved in the acid with a hissing sound and rise of temperature, and the solution finally set to a solid mass. Water was added and the temperature raised to boiling. During the boiling some decomposition was indicated by an escape of carbon dioxide. The solution on cooling deposited the nitro compound as a dark orange, sandy precipitate. After several recrystallizations from dilute acetic acid, it was obtained in orange, sandy crystals, melting with decomposition at about 302° (cor.). Yield, very poor.

Found. N, 22.9. Calculated for $C_{11}H_9O_6N_5$: N, 22.8

It is soluble in boiling water, very slightly soluble in boiling alcohol, in ether or in nitrobenzene. In aqueous caustic alkalies, it dissolves to a dark orange solution, from which it is precipitated slowly by saturation with carbon dioxide, more rapidly by acidification with acetic acid. The positions of the nitro groups were not determined, but it seems most likely that they are 6 and 8.

Bromo-7-acetamino-2-methyl-4-quinazolone. — The acetaminoquinazolone was suspended in dilute (50 per cent.) acetic acid and the mixture warmed Bromine was then added carefully to the warm solution. The reaction was vigorous, hydrobromic acid being evolved and the quinazolone dissolved. Soon thereafter the bromoquinazolone began crystallizing from the hot solution in minute needles. The solution was cooled, water added, the precipitate filtered out, washed, and recrystallized from dilute acetic acid or from a mixture of alcohol and acetic acid, in both of which it is rather difficultly soluble. It was thus obtained in minute needles, practically colorless, which began to darken at about 287° (cor.) and melted at 292° (cor.).

Found: N, 14.1; Br, 27.75. Calculated for $C_{11}H_{10}O_2N_3Br$: N, 14.2, Br, 27.03.

It is difficultly soluble in boiling alcohol. The use of a large excess of bromine in the above method of preparation gave the same product.

Bromo-7-amino-2-methyl-4-quinazolone. — The acetyl derivative just described was boiled for about an hour with ten per cent. potassium hydroxide solution, the solution cooled, diluted, filtered, and the filtrate saturated with carbon dioxide. The light yellow flocculent precipitate which separated was washed with water and purified by two crystallizations from alcohol. Light yellow flaky crystals were obtained, melting at 272–3° (cor.).

Found: N, 16.55. Calculated for $C_9H_8ON_3Br$: N, 16.53.

The substance is tribo-electric. It is moderately soluble in cold alcohol, easily in hot. It also dissolves in hot water, in warm nitrobenzene or isoamyl alcohol, but is apparently insoluble in ether, carbon tetrachloride or chloroform. The position of the bromine was not determined. Probably it is at 6.

7-Formamino-2-methyl-4-quinazolone, $HCONH.C_6H_3.CO.NH.C(CH_3) : N$.—7-Amino-2-methyl-4-quinazolone was boiled for four hours with excess of glacial formic acid, the excess of acid distilled off, the residual solution diluted, precipitated with sodium carbonate, and the precipitate crystallized from water. Colorless feathery crystals resulted, darkening at about 300°, softening in the neighborhood of 335°, and melting finally at 339–40° (cor.).

Found: N, 20.46. Calculated for $C_{10}H_9O_2N_3$: N, 20.69.

On standing a few days with ammoniacal silver nitrate solution to which a little sodium hydroxide has been added, it gives a silver mirror.

7-Propionamino-2-methyl-4-quinazolone, prepared in similar fashion, from the aminoquinazolone and propionic anhydride, crystallizes from water in long, white, silky needles, softening at about 317–20°, and melting at 326–7° (cor.).

Found: N, 18.48. Calculated for $C_{12}H_{13}O_2N_3$: N, 18.18.

It is tribo-electric and rather difficultly soluble in water or alcohol. In the latter solvent, it is much less soluble than the free aminoquinazolone. In hot, dilute organic acids, it is moderately soluble.

7-Hydroxy-2-methyl-4-quinazolone, $HO.C_6H_3.CO.NH.C(CH_3) : N$.—The 7-amino-2-methyl-4-quinazolone was dissolved in dilute hydrochloric acid and treated at 0° with the calculated amount of sodium nitrite in aqueous solution. Upon completion of the reaction, the mixture was diluted with water and boiled. Nitrogen was evolved freely and the color of the solution changed from yellow to orange. When the evolution of nitrogen ceased, the solution was allowed to cool. A small amount of flaky precipitate separated, but without removing this the mixture was neutralized with sodium carbonate. A voluminous yellow precipitate resulted. As we failed to get good crystals of this from any of the ordinary solvents, it was treated with moderately strong hydrochloric acid, which dissolved the greater part of it. The insoluble, dark orange portion was filtered out, and the filtrate neutralized with sodium carbonate. The light brown precipitate thus produced was again dissolved in hydrochloric acid, the solution filtered, and the filtrate reprecipitated with sodium carbonate. It was then dissolved in caustic alkali, yielding a red solution, reprecipitated with acetic acid, and dried. As thus purified, it formed a light brown powder, beginning to darken at about 345°, but not melting at that temperature.

Found: N, 16.28. Calculated for $C_9H_8O_2N_2$: N, 15.91.

It dissolves in hot alcohol or hot dilute acetic acid, but does not crystallize well from either solvent. It is soluble to a red solution in potassium hydroxide, and is reprecipitated from this solution by acetic acid but not by carbon dioxide. It is insoluble in ether, chloroform, carbon tetrachloride, benzene, toluene or acetone, but dissolves in hot isoamyl alcohol, aniline or nitrobenzene.

That portion of the original reaction product which was insoluble in the hydrochloric acid and dark orange in color, dissolved in potassium hydroxide solution with a red color, and when reprecipitated with hydrochloric acid came down in a gelatinous, colloidal condition which could not be further purified because of the small amount of material available.

7-Acetoxy-2-methyl-4-quinazolone, $CH_3COO.C_6H_3.CO.NH.C(CH_3) : N$.—On boiling the above 7-hydroxyquinazolone for an hour with excess of acetic anhydride, a reddish brown solution was obtained. This was cooled, diluted, and neutralized with sodium carbonate, giving a fine light brown precipitate which, on crystallization from alcohol, appeared in large pale brownish needles, softening at about 262° and melting at 266° (cor.).

Found:	C, 60 53;	H, 4.83;	N, 13.06.
Calculated for $C_{11}H_{10}O_3N_2$:	C, 60.55;	H, 4.60;	N, 12.84.

7-Cyano-2-methyl-4-quinazolone, $NC.C_6H_3.CO.NH.C(CH_3) : N$.—The 7-amino-2-methyl-4-quinazolone was diazotized and boiled with copper potassium cyanide solution. The precipitate was filtered out, washed with water, dried and extracted with carbon tetrachloride, to free it from metallic cyanides. On evaporating the carbon tetrachloride, a colorless crystalline mass remained, which was further purified by two crystallizations from alcohol, and then appeared in colorless feathery needles, melting at about 303–4° (cor.), and not volatile with steam.

Found: N, 22.0. Calculated for $C_{10}H_7ON_3$: N, 22.6.

The unsatisfactory character of this analytical result is due partly to the fact that the yield of product in the above reaction is very small and we did not have sufficient to run a good analysis. From 5 g. of the amino compound, the yield of pure cyano compound was only 0.1 g. This was particularly disappointing, as we had hoped to obtain sufficient to saponify to the corresponding acid, for the latter has already been described in a previous paper from this laboratory.[1]

7-Acetamino-2,3-dimethyl-4-quinazolone,

$CH_3CONH.C_6H_3.CO.N(CH_3).C(CH_3) : N$, was prepared from 4-acetamino acetanthranil in essentially the same manner as the monomethyl compound, using methylamine instead of ammonia. Recrystallized from alcohol, it forms colorless silky needles, melting at 284° (cor.).

---

[1] Bogert, Wiggin and Sinclair, THIS JOURNAL, 29, 87 (1907).

Found: N, 18.5. Calculated for $C_{12}H_{13}O_2N_3$: N, 18.2.

It is soluble in hot water or in alcohol, slightly soluble in acetone, insoluble in ether, carbon tetrachloride or ligroin.

7-Amino-2,3-dimethyl-4-quinazolone.—The above acetyl derivative was heated for about an hour with 10 per cent. potassium hydroxide solution in excess, the solution filtered hot, and the filtrate allowed to cool. The free base separated as the filtrate cooled in rosettes of fine colorless silky needles (or short heavy prisms, if the cooling occurred very slowly), which darkened on exposure to the air, and on recrystallization from water melted at 224° (cor.).

Found: N, 22.36. Calculated for $C_{10}H_{11}ON_3$: N, 22.22.

The substance is easily soluble in warm water, alcohol or benzene, slightly soluble in chloroform, insoluble in ether or ligroin. On attempting, by means of the diazo reaction, to replace the amino group by an OH, the yield of product was so small that the effort was abandoned.

Chloroplatinate.—Red crystals.

Found: Pt, 24.6. Calculated for $(C_{10}H_{11}ON_3)_2PtCl_6$: Pt, 24.7.

7-Acetamino-2-methyl-3-ethyl-4-quinazolone. — 4-Acetaminoacetanthranil was heated with an aqueous ethylamine solution. The anthranil dissolved and, on cooling, the quinazolone separated in colorless, glistening, pearly plates. Recrystallized from alcohol, it formed short colorless needles, melting at 254° (cor.).

Found: N, 17 07. Calculated for $C_{13}H_{15}O_2N_3$. N, 17.14.

It crystallizes from water in clusters of long, colorless, silky needles, slightly soluble in cold, readily in warm alcohol.

*7-Acetamino-2-methyl-3-*n*-propyl-4-quinazolone.* — 4-Acetaminoacetanthranil was added to the *n*-propylamine diluted with a little water, and the mixture heated. The anthranil dissolved and, on cooling, the quinazolone precipitated in colorless, silky needles. Recrystallized from water, rosettes of needles were obtained, melting at 206–7° (cor.).

Found: N, 16.46. Calculated for $C_{14}H_{17}O_2N_3$: N, 16.22.

*2,4-Diacetamino-*sec.*butylbenzamide*, $(2,4)(CH_3CONH)_2C_6H_3CONHC_4H_9$. —No condensation could be effected with the anthranil and a dilute aqueous solution of secondary butylamine (2-aminobutane), but when the anthranil was boiled with the pure amine, colorless needles separated from the solution on cooling. These needles were purified by repeated crystallization from dilute alcohol, giving finally a m. p. of 235° (cor.). Dried at 100–20°, the substance was analyzed with the following result:

Found: N, 14.61. Calculated for the quinazolone ($C_{15}H_{19}O_2N_3$): N, 15.38; for the intermediate amide ($C_{15}H_{21}O_3N_3$): N, 14.43.

The product is thus apparently the amide and not the expected quinazolone. It forms short, colorless needles. Boiled with water, these crystals dissolve, but do not separate again as the solution cools. Treated with potassium hydroxide solution, acetanthranilic acid results and not the quinazolone.

7-Acetamino-2-methyl-3-isoamyl-4-quinazolone.—When 4-acetaminoacetanthranil was heated with a dilute aqueous solution of isoamylamine, no quinazolone was obtained. The anthranil was therefore added directly to the pure undiluted amine and the mixture heated. The anthranil dissolved, but nothing separated from the solution on cooling. It was then diluted and heated, and on cooling the quinazolone separated as a white, flaky precipitate. Recrystallized repeatedly from dilute alcohol, it was obtained in rosettes of colorless, silky, feathery needles, melting at 288° (cor.), soluble in alcohol, difficultly soluble in cold water, moderately soluble in hot.

Found: N, 14.76. Calculated for $C_{16}H_{21}O_2N_3$: N, 14.63

7-Acetamino-2-methyl-3-phenyl-4-quinazolone was obtained by heating the anthranil and aniline together. Recrystallized from alcohol, it formed minute, colorless, pearly octahedra, melting at 276° (cor.).

Found: N, 14.24. Calculated for $C_{17}H_{15}O_2N_3$. N, 14.33.

It is apparently insoluble in ether, chloroform, acetone or water; very slightly soluble in hot carbon tetrachloride; but dissolves readily in hot alcohol or nitrobenzene.

*7-Acetamino-2-methyl-3-*p*-anisyl-4-quinazolone.*—1.09 g. of 4-acetaminoacetanthranil and 0.61 g. *p*-anisidine were intimately mixed and the mixture heated. At 55° it formed a thick paste, gradually growing more fluid up to 90° when the mass solidified The temperature was then raised to 100° and the salmon-colored mass, after a short heating at this temperature, allowed to cool. Crystallized from dilute alcohol, flesh-colored, glistening octahedra were obtained, melting at 273° (cor.), easily soluble in hot alcohol, apparently insoluble in water, ether or chloroform.

Found. N, 13.2. Calculated for $C_{18}H_{17}O_3N_3$: N, 13.0.

*7-Acetamino-2-methyl-3-*p*-phenetyl-4-quinazolone.*—0.7 g. *p*-phenetidine was dissolved in dilute alcohol, 1 g. 4-acetaminoacetanthranil added, and the temperature raised to boiling. No condensation took place. But when the two substances were heated together dry at 95°, in the same proportion, the mixture first liquefied, then solidified (at about 80°). The crude product on crystallization from dilute alcohol gave clusters of fine short needles, of a slight pinkish cast, and melting at 259° (cor.).

Found: C, 67.50; H, 5.88; N, 12.66. Calculated for $C_{19}H_{19}O_3N_3$: C, 67.66; H, 5.64; N, 12.46.

It is difficultly soluble in hot water or in carbon tetrachloride, insoluble in ether, but dissolves in boiling benzene, and is easily soluble in warm chloroform, ethyl or isoamyl alcohol. The structure of this compound recalls rather remotely that of phenacetine, but its physiological properties have not been studied.

4-Acetaminoacetanthranil and p-*Aminobenzonitrile.*—2.18 g. of the anthranil were heated with 1.18 g. of the nitrile. At 85° the mixture formed a thick paste, which became thinner as the temperature rose. At 140° the heating was interrupted and the melt allowed to cool. When the crude product was crystallized from dilute alcohol, rosettes of pale yellowish, downy needles were obtained, very strongly tribo-electric and softening at about 240°. Recrystallized until colorless, these needles melted at 258° (cor.) with decomposition.

Found: N, 13.36. Calculated for the quinazolone ($C_{18}H_{14}O_2N_4$): N, 17.61.

The product is evidently not the quinazolone. Dried three hours at 130–60° and again analyzed, the nitrogen percentage was found to be 13.41, *i. e.*, practically unchanged.

The substance is soluble in alcohol, insoluble in water. In dilute alcohol, it gives an opalescent solution. Boiled with dilute (10 per cent.) potassium hydroxide solution, it dissolves with copious evolution of ammonia, but no precipitate results when the solution is acidified with acetic or hydrochloric acid. Attempts to prepare an acetyl derivative were unsuccessful.

In another experiment, the constituents were heated to a somewhat higher temperature (170°), but the product showed the same melting point (258° cor.) and approximately the same nitrogen percentage (found, 12.96 per cent.).

7-Acetamino-2-methyl-3-α-naphthyl-4-quinazolone.—1.09 g. 4-acetamino acetanthranil and 0.715 g. α-naphthylamine were heated together. The mixture became pasty at about 50°, quite fluid at 80–100°, thickening again at 120°. The heating was carried to 150° and the melt then allowed to cool. When cold it was brittle and highly tribo-electric. Treated with cold chloroform, it dissolved and then light-colored flakes gradually separated. On warming, this precipitate increased. It was filtered from the warm solution, washed with ether and dried. The product is a pale gray powder, melting at 256° (cor.).

Found: N, 12.05. Calculated for $C_{21}H_{17}O_2N_3$: N, 12.24.

It appears to be less soluble in hot than in cold chloroform. It is soluble also in methyl or ethyl alcohol, or in glacial acetic acid, but insoluble in ether.

7-Acetamino-2-methyl-3-amino-4-quinazolone.—On mixing 4-acetamino-acetanthranil and hydrazine hydrate in equimolecular proportion and heating the mixture to boiling, the anthranil dissolved, and soon there separated from the boiling solution fine, colorless, glistening needles which, when recrystallized from 95 per cent. alcohol, carry a molecule of water of crystallization, the anhydrous base melting at 268° (cor.).

Found: H_2O, 7.31. Calculated for $C_{11}H_{12}O_2N_4.H_2O$: H_2O, 7.2
Found: N, 24.38. Calculated for $C_{11}H_{12}O_2N_4$: N, 24.14.

The water of crystallization is not easily driven out at 110°, but can be removed by drying at 125–30°. The anhydrous base is practically insoluble in ether, benzene, water or cold alcohol; difficultly soluble in chloroform; moderately soluble in hot, dilute alcohol; easily soluble in warm nitrobenzene.

When an equimolecular mixture of the above quinazolone and diacetosuccinic ester, dissolved in glacial acetic acid, was boiled for an hour, no condensation occurred. When a little acetic anhydride was added to the glacial acetic acid solution, the only effect was acetylation of the amino group. The two substances were therefore fused together without solvent. A brown paste resulted at about 210°, considerable acetic acid being evolved during the fusion. When cold, the mass was pulverized, and the tan-colored product crystallized thrice from alcohol, giving short, tan-colored needles, melting at 253–4° (cor.) which, on further purification, proved to be only the unchanged quinazolone. The reaction therefore involved only the breaking down of the diacetosuccinic ester and no condensation to a pyrrole derivative. We had expected, from the investigations of Bülow[1] and our own experience with —N — NH_2 quinazolones, to get the pyrrole compound.

Hydrochloride.—The aminoacetaminoquinazolone was suspended in ether and the solvent saturated with dry hydrogen chloride. The free base was thus changed to the hydrochloride and remained insoluble in the ether. It was filtered out, washed with ether, and dried *in vacuo* over potassium hydroxide.

Found: N, 19.65. Calculated for $2C_{11}H_{12}O_2N_4.3HCl$: N, 19.53.

Short, colorless needles, darkening somewhat at about 305°, and melting with vigorous decomposition at 312° (cor.).

When the aminoquinazolone was dissolved in 95 per cent. alcohol and the solution saturated with dry hydrogen chloride, no hydrochloride was formed, the unchanged quinazolone itself precipitating.

2,4-Diacetaminobenzohydrazide, $(2,4)(CH_3CONH)_2C_6H_3CONHNH_2$.—In the interaction of the acetaminoacetanthranil and hydrazine hydrate (in 50 per cent. aqueous solution), if the anthranil is added to the hydrazine hydrate solution without heating, it remains in suspension for a few seconds, then heat is evolved and finally a snowy pasty mass is formed made of fine short needles. If water be now added and the mixture boiled, the aminoacetaminoquinazolone described above is formed.

---

[1] *Ber.*, 39, 2621, 3372 (1906), etc.

If, on the other hand, these first crystals be filtered out, recrystallized from alcohol, and dried at 80°, the hydrazide is the product.

Found: N, 22.43. Calculated for $C_{11}H_{14}O_3N_4$: N, 22.4.

Dried six hours at 120–40°, no loss of weight occurred and no important change in the nitrogen percentage (found, 22.55 per cent. nitrogen). The crystals melt at the same point as the 7-acetamino-2-methyl-3-amino-4-quinazolone, probably passing into this by loss of water at higher temperatures.

3,7-Diacetamino-2-methyl-4-quinazolone, prepared from the aminoacetaminoquinazolone by the action of acetic anhydride, crystallizes from water with water of crystallization. These hydrated crystals melt down at 100°. From alcohol, it crystallizes in minute, colorless crystals, melting at 304° (cor.).

Found: N, 20.34 and 20.44. Calculated for $C_{13}H_{14}O_3N_4$: N, 20.44.

Excess of acetic anhydride causes no further acetylation.

3,7-Diamino-2-methyl-4-quinazolone. — 7-Acetamino-2-methyl-3-amino-4-quinazolone was boiled for half an hour with dilute (10 per cent.) potassium hydroxide solution. On cooling, colorless, silky needles were deposited in clusters in such amount that the whole mass solidified. These crystals were washed with water and recrystallized from dilute alcohol, melting then at 238° (cor.).

Found: N, 29.7. Calculated for $C_9H_{10}ON_4$: N, 29.5

7-Acetamino-2-methyl-3-anilino-4-quinazolone,

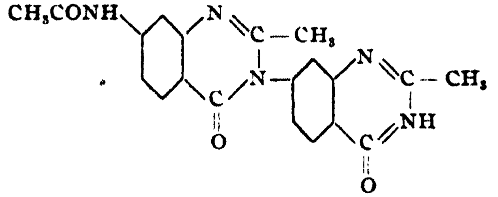
$CH_3CONH.C_6H_3.CO.N(NHC_6H_5).C(CH_3):N$. — 4-Acetaminoacetanthranil was added to an equimolecular amount of phenylhydrazine in alcoholic solution and the mixture heated to boiling. A clear yellow solution resulted which gradually changed to dark red on continuing the heating. After a half hour's boiling, the solution was concentrated and allowed to cool. Nodules of fine yellow needles were deposited. After several recrystallizations from alcohol, they appeared as colorless, feathery needles, softening at about 208°, and melting at 214° (cor.).

Found: N, 18.4. Calculated for $C_{17}H_{16}O_2N_4$: N, 18.2.

The substance is soluble in hot water, benzene, chloroform, acetone, ethyl or isoamyl alcohol, or in nitrobenzene, less readily in ether or in carbon tetrachloride.

When the anthranil was added to a slight excess of pure and undiluted phenylhydrazine and the mixture gently warmed, the anthranil dissolved and the reaction proceeded with violent ebullition even when the source of external heating was immediately removed at the beginning of the reaction. It is likely that deeper-seated changes accompanied this reaction, as we failed to isolate any of the above anilino derivative among the products.

7-Acetamino-2-methyl-3 : 7′-[2′-methyl-4′-quinazolone]-4-quinazolone,



7-Amino-2-methyl-4-quinazolone and 4-acetaminoacetanthranil, in equimolecular proportion, were intimately mixed and the mixture heated gradually to 250°. The melt on cooling formed a brown, porous, brittle mass, giving a yellow powder when pulverized. This powder was dissolved in alcohol, the solution treated with bone-black twice, and the filtrate then concentrated. Short, thick, light yellow needles crystallized out, darkening at about 330° and melting at 335° (cor.).

Found. C, 63.86; H, 4.86; N, 18.61. Calculated for $C_{20}H_{17}O_3N_5$. C, 64.00; H, 4.53; N, 18.67.

The compound dissolves in boiling water, in alcohol or in nitrobenzene. It is very slightly soluble in carbon tetrachloride, benzene, ligroin or ether, but somewhat soluble in acetone. It dissolves also in potassium hydroxide solutions and is reprecipitated therefrom by saturation with carbon dioxide. The alcoholic solution of the substance shows a greenish fluorescence.

III. Quinazolones from 5-Acetaminoacetanthranil.

6-Acetamino-2-methyl-4-quinazolone, prepared from the 5-acetamino acetanthranil and ammonia, is much less readily soluble in alcohol than the 7-acetamino isomer. It crystallizes from this solvent in clusters of small, coarse, colorless needles or prisms, melting at 350° (cor.).

Found: N, 19.33. Calculated for $C_{1}H_{11}O_2N_3$. N, 19.35.

6-Amino-2-methyl-4-quinazolone.—The acetyl derivative was boiled with excess of 10 per cent. potassium hydroxide solution, and the solution then precipitated by carbon dioxide. The precipitate crystallized from water in rosettes of long, colorless, highly refracting needles, which began to darken in the neighborhood of 300°, softened somewhat at about 304°, and melted finally at 314–5° (cor.).

Found: N, 23.92. Calculated for $C_9H_9ON_3$: N, 24.0.

At 70–80°, the crystals lose their luster, although they do not carry any water of crystallization. The compound tends to darken on standing. It is insoluble or difficultly soluble in ether, ligroin, chloroform or benzene, but dissolves in ethyl or isoamyl alcohol, acetone or nitrobenzene.

6-Acetamino-2,3-dimethyl-4-quinazolone. — 5-Acetaminoacetanthranil was added to a dilute aqueous solution of methylamine and the mixture heated. The anthranil first dissolved and then the quinazolone separated from the hot solution in colorless, silky needles, soluble in alcohol, and melting at 278° (cor.).

Found: N, 18.22. Calculated for $C_{12}H_{13}O_2N_3$: N, 18.18.

6-Acetamino-2-methyl-3-ethyl-4-quinazolone was prepared similarly, using ethylamine instead of methylamine. When the anthranil and ethylamine were heated together (the latter being used in aqueous solution), a clear solution was obtained, from which nothing separated on further heating or on cooling. A small amount of potassium hydroxide was added, the solution again boiled, and on long standing the quinazolone finely separated in long, colorless, silky needles which, after recrystallization from water, melted at 229° (cor.).

Found: N, 17.43. Calculated for $C_{13}H_{15}O_2N_3$: N, 17.14.

The crystals are highly refracting, and dissolve in hot water or in alcohol.

*6-Acetamino-2-methyl-3-*n*-propyl-4-quinazolone*, from the anthranil and *n*-propylamine, crystallizes from water in long, colorless, silky needles, melting at 181° (cor.).

Found: N, 16.45. Calculated for $C_{14}H_{17}O_2N_3$: N, 16.22.

6-Acetamino-2-methyl-3-phenyl-4-quinazolone.—The anthranil and pure aniline were heated together at 110°, and the product purified by repeated crystallization from dilute alcohol. It forms brownish plates, melting at 255° (cor.), very difficultly soluble in boiling water, readily in hot alcohol.

Found: N, 14.43. Calculated for $C_{17}H_{15}O_2N_3$: N, 14.33.

6-Acetamino-2-methyl-3-amino-4-quinazolone.—The anthranil was added to a dilute aqueous hydrazine hydrate solution and the mixture heated to boiling. The anthranil dissolved and, on cooling, the quinazolone crystallized out in rosettes of colorless, silky needles, which were washed with water and recrystallized from it, when they melted at 262–3° (cor.). The crystals are soluble in hot water or in alcohol.

Found: N, 24.29. Calculated for $C_{11}H_{12}O_2N_4$: N, 24.14.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, June, 1910.

ETHYL TANNATE.

BY R. J. MANNING.

Received June, 1910.

Of the naturally occurring tannins gallotannic acid, obtained from gallnuts and many other sources, is the most important and best known. Strecker[1] claims that gallotannic acid is a glucoside of gallic acid as it yielded gallic acid and glucose on hydrolysis. Schiff[2] synthesized digallic acid from gallic acid by means of phosphorus oxychloride and claims that digallic acid and gallotannic acid are isomers. If this were so, gallotannic acid would have a formula $C_{14}H_{10}O_9$ and on hydrolysis would yield no glucose. On account of the difficulty in purifying the tannin, determinations of its composition vary with different experimenters. I have prepared a crystalline ester and through it have obtained satisfactory analyses giving the composition of gallotannic acid and considerable information about it.

---

[1] *Ann.*, 90, 340.

[2] *Ibid.*, 170, 49.

Description of the Gallotannic Acid Used.

The material used in these experiments was obtained through Lyman Bros., Toronto, from the German firm of Schering, and came in the form of light whitish brown flakes; extracted with ether in a Soxhlet, all dissolved, leaving a slight brown stain on the shell, soluble in boiling water. It was purified by the method described by Walden:[1] 100 grams of the commercial tannin were dissolved in 250 grams of amyl alcohol (which must contain a little water) and 350 grams of ether were added; no precipitate appeared. The tannin was then thrown down by gasoline, filtered and dried in a vacuum desiccator over sulphuric acid. So purified, it formed a whitish, rather heavy powder.

The crude sample of tannin contained a trace of gallic acid detected by the potassium cyanide method;[2] the purified product was free from this if excess of gasoline were not added during purification, and in every respect, except solubility, behaved like gallotannic acid as described in Allen's "Commercial Organic Analysis."[3]

Hydrolysis.—A dilute aqueous solution, after boiling for half an hour, reduced Fehling's solution (glucose) and gave a distinct red with potassium cyanide (Young's test for gallic acid); the same result is obtained by boiling for a moment with dilute hydrochloric acid. After long boiling with calcium carbonate while a current of air passed through the solution, the blue coloration changing to red with acids (which is characteristic of gallic acid) was observed.

Behavior with Reagents.—*Arsenic acid* in 5 per cent. alcoholic solution, warmed with its own volume of a 10 per cent. solution of the tannin, solidified to an insoluble jelly, which on standing in the air dried up to a garnet colored mass. *Ammonium molybdate* and *potassium ferricyanide*, reddish colorations; *lime water*, white precipitate quickly turning blue; *ferric chloride*, blue-black precipitate, soluble in much water; *lead acetate or nitrate*, white precipitate in not too dilute solutions; *silver nitrate*, silver mirror on warming; *copper sulphate*, greenish blue gelatinous precipitate turning black on warming; *potassium permanganate* in alkaline solution, red-brown precipitate, dissolving on warming to a yellow-brown solution which becomes wine-red in the air; dilute *sulphuric acid* and dilute *hydrochloric acid*, and *concentrated salt* solutions form precipitates in moderately concentrated solutions of the tannin, which dissolve again on adding water.

---

[1] *Ber.*, 31, 3167 (1898).

[2] S. Young, *Chem. News*, 48, 31.

[3] Vol. III, Part I, pages 35–38 (1900).

Solubility.--My preparation was soluble in water, glycerol, ethyl acetate, and acetone; slightly soluble in anhydrous amyl alcohol, ether or ethyl alcohol; very slightly soluble in carbon disulphide, benzene and gasoline. It is quite insoluble in chloroform (the gallotannic acid and chloroform were shaken together and filtered, but the filtrate gave no coloration whatever with ferric chloride).

Allen[1] says that gallotannic acid is soluble in six parts of cold water; my preparation was much more soluble. In an experiment in which the tannin and water were shaken together in a thermostat at 0°, many successive portions of tannin kept dissolving until the liquid was a thick sirup, and further addition of the solid balled together and dissolved with extreme slowness. In the end the perfectly clear brownish sirup contained less than one and a half grams of water to one of tannin. At 32° the saturated sirup was still thicker, and contained more than two grams of tannin to one of water.

The solubility of tannin in ether, amyl alcohol, and ethyl acetate, is greatly increased by the addition of a trace of water, as shown by the following data:

One gram of	Dissolved at 15°
Ethyl acetate (Kahlbaum)............	...... 0.2 g. tannin
" " with 5 per cent. water by volume	.... 2.5 " "
Amyl alcohol normal (Kahlbaum).......	.... 0.1 " "
" " with 5 per cent. water by volume ..	.... 0.84 " "

The solubility of mannose, glucose, galactose, cane sugar and of the glucosides, saponin, salicin, and amygdalin in amyl alcohol, acetone, and in ethyl acetate, is also much increased by the addition of a trace of water but not so markedly as in the case of tannin. The solubility of the alkaloids, strychnine and brucine, in ethyl acetate and in acetone, on the other hand, is not markedly increased by the addition of water.

In these solubility determinations the method of analysis for gallotannic acid was that described by F. Jean,[2] involving titration with iodine in alkaline solution.

Analysis of Gallotannic Acid.

To insure perfect dryness the tannin was heated in a hot air bath at 110° for two hours.

(*a*) The elementary analysis gave the following results:

---

[1] *Commercial Organic Analysis*, 3rd Ed., Vol. III, Part I, page 34.

[2] *Chem. Centr.*, 1900, I, 1107.

Calculated for $C_{41}H_{32}O_{20}$. C, 52.35; H, 3.40.
Found: C, 52.4, 52.25; H, 3.45, 3.49.

(*b*) To estimate the glucose in tannin, the following procedure was adopted: 0.2 to 0.5 gram of the tannin was boiled with 200 cc. water and 25 cc. of 10 per cent. hydrochloric acid for an hour. As gallic acid has a marked reducing action on Fehling's solution, it was removed by extraction with ether, and as glucose itself is somewhat soluble in water-saturated ether, the extraction was carried on quantitatively and a correction applied as follows:

From 0.1 to 0.25 gram glucose was mixed with 0.5 to 1.2 grams ethyl gallate and the mixture dissolved in 200 cc. water and 25 cc. of 10 per cent. hydrochloric acid. After boiling the solution for an hour, it was made up to 100 cc. and extracted six times by shaking up for ten minutes each time with 50 cc. of ether. After the sixth extraction, all the gallic acid formed by the hydrolysis of the ether except a slight trace had been removed. The following percentages of the original glucose were found by analysis in the aqueous layer:

Glucose	78 9	79 0	78 8	78. 6 per cent

Hence the boiled solution of tannin was extracted six times with ether, the free hydrochloric acid neutralized with sodium carbonate, the glucose estimated and the results multiplied by 100/79.

The analysis gave glucose 19 0, 18 79 per cent Calculated on the assumption that one formula weight of the tannin on hydrolysis gives one formula weight of glucose: 19.1 per cent

(*c*) Formula weight determinations from the boiling point of solutions:

Water as solvent.	813	843	922	1025	1500
Acetone as solvent	1672	2023	1500	1450	
Water as solvent (from freezing point)	1957	1942	1769	1956	1972

Calculated for $C_{41}H_{32}O_{20}$. 940

Preparation of the Ethyl Ester of Gallotannic Acid.

50 grams of the tannin were dissolved in 250 cc. of Kahlbaum's 99.8 per cent. ethyl alcohol. After introducing the light brown solution into a 500 cc. flat-bottomed flask, hydrogen chloride gas, dried by passing through 18 inches of pumice stone moistened with sulphuric acid, was bubbled through for at least two and a half hours. During the operation the temperature of the liquid rose to about 60°. By cooling the solution during the passage of the gas through it, the yield was diminished, while applying heat to the flask did not noticeably increase the amount of the ester formed.

The dark brown sirup left after the passage of the hydrogen chloride gas was evaporated in a large porcelain evaporating dish until quite thick, and Kahlbaum's lime-free barium carbonate added in excess. The sticky mass was extracted three times with anhydrous ether, the resulting greenish brown ethereal liquid allowed to evaporate, and the residue heated for some hours in a water bath. A dark greenish brown powder remained.

The crude ethyl tannate so obtained was purified by extraction with chloroform in a Soxhlet for two days. This leaves behind the coloring matter and unaltered tannin but dissolves any ethyl gallate as well as the ethyl tannate; hence the necessity of using tannin as free as possible from gallic acid. During the extraction the ethyl tannate separated out of the chloroform in the form of pale yellow spherical nodules of about 2 mm. in diameter. The yield was about 40 per cent. of the tannin used.

In the hope of obtaining a better yield, 50 cc. of benzene[1] were added to the dark brown solution through which the hydrochloric acid gas had been passed, the whole well shaken and the benzene distilled off. After three successive treatments with benzene, the liquid left in the distilling flask was evaporated and treated with barium carbonate and ether as before. This method gave no better yield and was therefore not used again.

Description of the Ethyl Tannate.

On splitting open these nodules, they were seen to consist of a mass of light yellow shining crystals radiating from a common center. Their melting point was 157° (ethyl gallate melts at 141°).[2] They were readily soluble in ether, alcohol and water; slightly soluble in chloroform; insoluble in gasoline and in carbon bisulphide. Their aqueous solution resembled a solution of tannin in its reactions with ammonium molybdate, lead nitrate or acetate, silver nitrate, copper sulphate, and potassium permanganate. With potassium cyanide the aqueous solution of ethyl tannate always gave a slight red color indicating the presence of traces of gallic acid or its ester.

Analysis of the Nodules.

(*a*) *Elementary Analysis.*—The substance was mixed with a little carefully dried red lead and ignited in a porcelain boat.

The analysis gave:	C, 52.3	52.4	52.35:	H, 5.25	5.11	5.25
Calculated for $C_{51}H_{62}O_{31}$:	52.30			5.30		

(*b*) *Loss of Water on Heating.*—To estimate the percentage of water, the nodules were heated in an air bath to 125–135° for two hours. On first heating they became rather sticky, but did not melt completely, and on continued heating became drier again but showed a tendency to turn brown and to sublime. Hence care had to be taken not to allow the temperature to rise over 135°.

The analysis gave: 7.6, 7.5, 7.8 water; calculated for $C_{51}H_{52}O_{26}.5H_2O$: 7.69 per cent.

---

[1] *J. Chem. Soc.*, 88, 852 (1905).

[2] Etti, *Ber.*, 11, 1882.

(*c*) *Ethoxyl Determination.*—The method used was that of Zeisel as described in Meyer and Tingle's "Estimation of Organic Radicles," pp. 34–48. In some of my determinations the precipitate of silver iodide was brownish instead of yellow. The results with these colored precipitates varied widely, being too large, and hence were rejected. It was found afterward, however, that if the brown silver iodide precipitates in these high results were boiled for five minutes with 100 cc. of 15 per cent. nitric acid, filtered and weighed, the precipitates regained their normal color and the new results agreed with those not rejected. This treatment with nitric acid does not perceptibly affect the pure silver iodide.

OC_2H_5 found: 19.24, 19.32, 19.39, 19.55, 19.55 per cent.; calculated for $C_{41}H_{27}O_{21}(OC_2H_5)_5.5H_2O$[1]: 19.23 per cent.

(*d*) *Hydrolysis of the Ester and Estimation of the Glucose.*—2 grams of the ester were boiled with 100 cc. water for two hours with a return condenser and then 25 cc. distilled off. This distillate gave no trace of alcohol when tested by the iodoform method.[1] If, however, previous to the distillation, 10 cc. of dilute hydrochloric acid or of dilute caustic potash were added to the distilling flask, the distillate then gave, especially in the latter case, a distinct deposit of iodoform.

The freshly prepared solution of ethyl tannate reduced Fehling's solution slightly; but the solution which had been boiled with acid or with caustic potash reduced Fehling's solution readily and gave a marked potassium cyanide test for gallic acid. The products of the hydrolysis are therefore ethyl alcohol, glucose, and gallic acid.

The glucose was estimated by the same method as was used for the estimation of glucose in the gallotannic acid and the same correction was applied.

The analysis gave: 15.37, 15.42, 15 51, 15.13 per cent glucose. Calculated on the assumption that one formula weight ($C_{51}H_{62}O_{31}$) of the ester on hydrolysis gives one formula weight of glucose: 15.38 per cent.

(*e*) *Estimation of the Gallic Acid.*—0.2 to 0.3 gram of the ethyl tannate was hydrolyzed by boiling with dilute hydrochloric acid as in the estimation of the glucose. The boiled solution was then diluted to 250 cc. and the gallic acid estimated by the iodine titration method of Jean.[2]

Gallic acid found: 72.56, 72.66, 72.8. Calculated on the assumption that one formula weight ($C_{51}H_{62}O_{31}$) of the ester on hydrolysis gives five formula weights of gallic acid: 72.64 per cent.

(*f*) *Formula-weight Determinations from Boiling Point of Solutions.*—

Acetone as solvent: 255, 280, 257.
Ethyl acetate as solvent: 362, 275, 300.
Chloroform as solvent: 1335, 1000, 1200, 1467.
Water as solvent (from freezing point): 301, 309.
Calculated for $C_{51}H_{62}O_{31}$: 1170

---

[1] *Z. anal. Chem.*, 9, 492.

[2] *Chem. Centr.*, 1900, I, 1107.

Comparing these results, it is seen that those given by the chloroform solution are several times greater than those given by the other solutions. The lower numbers might be explained by assuming that in all the solvents but chloroform there is a dissociation into anhydrous ester and water. To test this, 0.5 to 1.0 gram of the ester was dissolved in 50 cc. acetone and the solution dehydrated carefully by introducing 10 grams anhydrous calcium chloride. After filtering and washing the calcium chloride carefully with acetone, the filtrate was diluted up to 100 cc. and its boiling point determined, giving the following results:

Formula weight found· 950, 1050. Calculated for $C_{51}H_{32}O_{26}$: 1080.

Moreover, on evaporating this solution to dryness, an amorphous, dark brown, sticky mass was left, instead of the crystalline substance before obtained.

A Higher Hydrate of the Ester of Gallotannic Acid.

On the evaporation of solutions of ethyl tannate in ether, chloroform, alcohol, acetone, and ethyl acetate, only minute crystals were obtained. To get large crystals, a cold (15°) saturated aqueous solution of ethyl tannate, obtained without heat, was allowed to evaporate in a round-bottomed evaporating dish by being placed in the sunlight. Even at that temperature a partial decomposition of the ester into ethyl gallate and glucose took place. The ethyl gallate, being less soluble, crystallized out first as a top ring of pale yellow, steep rhombic crystals around the sides of the evaporating dish. At the bottom of the vessel, on almost complete evaporation, were found large, light brown crystals, many between one and two centimeters in length, with a sticky fluid containing the glucose.

An aqueous solution of these crystals behaved like a solution of the lower hydrate of ethyl tannate. They melted at 132°[1] and effloresced readily over sulphuric acid and slowly in the air. They lost their water of crystallization on being heated at 125–135° like the lower hydrate.

Analysis gave: 20.5, 20.7, 21.0 per cent. water. Calculated for $C_{51}H_{52}O_{26}.15H_2O$: 20 per cent.

Synthesis of Ethyl Tannate from Ethyl Gallate and Glucose.

20 grams ethyl gallate prepared according to Schiff's method[2] were ground up with 5–6 grams glucose and mixed to a thin paste with phosphorus oxychloride. After heating this paste in a water bath for two hours, during which time great quantities of hydrochloric acid were given off, a dark sticky mass remained. This was further dried by heating at 120° for a couple of hours, extracted with anhydrous ether, the ether solution evaporated, and the residue again extracted with chloroform in a Soxhlet for twenty-four hours. At the end of that period a light

---

[1] Hydrated ethyl gallate melts at 90°.

[2] Schiff, *Ann. Chem.*, 163, 215; 170, 72.

colored mass had settled out of the chloroform. By the fractional crystallization of its aqueous solution as previously described, the higher hydrate of the ethyl ester of gallotannic acid was obtained. This gave all the reagent tests for tannin, for glucose, and ethoxyl groups. It melted at 132°. The maximum yield I obtained was only about 5% of the theoretical.

Summary.

1. Two crystalline derivatives of tannin have been obtained. They are ethyl esters of gallotannic acid differing in the amount of water of crystallization. The previous analyses of gallotannic acid varied because crystalline derivatives were not known and therefore pure material was very difficult to obtain.

2. These esters were synthesized from alcohol and gallotannic acid and one of them was also synthesized from ethyl gallate and glucose.

3. Various analyses show that the formulas for these esters are $C_{41}H_{27}O_{21}(OC_2H_5)_5.5H_2O$ and $C_{41}H_{27}O_{21}(OC_2H_5)_5.15H_2O$, and that they are glucosides of gallic acid in which one formula weight of glucose and five formula weights of gallic acid are represented in one formula weight of the ester. This gives the formula $C_{41}H_{32}O_{26}$ for gallotannic acid.

4. Dissociation of the hydrated ester into water and anhydrous ester would account for the low formula-weight determinations in acetone, etc.

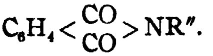
This work was done under the direction of Professor W. Lash Miller.

UNIVERSITY OF TORONTO

ACTION OF AMINES ON PHTHALIC ACID. VII.[1]

By J. Bishop Tingle and S. J. Bates

Received August 4, 1910

The work described in the earlier papers by the senior author and his colleagues has shown that the phthalamidic acids combine with amines to form salts, $RNHCOC_6H_4CO_2NH_3R'$. Secondary or tertiary amines, if they are not too negative, convert these salts into imides, $C_6H_4{<}\substack{CO\\CO}{>}NR$ or $C_6H_4{<}\substack{CO\\CO}{>}NR'$, whereas primary amines give rise to one or more of the following products: the amidic acid $R'NHCO C_6H_4CO_2H$, the amides $RNHCOC_6H_4CONHR$ or $C_6H_4(CONHR')_2$, and the imides formulated above. In the case of the secondary phthalamidic acids, $RNR'COC_6H_4CO_2H$, where R and R' may represent similar or dissimilar groups, the amine $R''NH_2$ behaves somewhat differently; it may cause hydrolysis of the original amidic acid to phthalic acid, or the group R″ may replace R or R′ in the amidic acid, giving $R''NHCOC_6H_4CO_2H$. This last acid may then eliminate water and form the imide  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>NR''$. The amidic acids of the aliphatic series[1] do not exhibit a similar series of reactions and consequently the formation of substituted imides, under the influence of amines, could only be ascribed to the influence of "the inherent nature of the benzene nucleus."

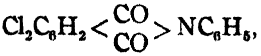
---

[1] The previous papers bearing on this subject have appeared as follows: Bishop Tingle and Cram, *Am. Chem. J.*, **37**, 596 (1907); Bishop Tingle and Lovelace, *Ibid.*, **38**, 642 (1907); Bishop Tingle and Rolker, THIS JOURNAL, **30**, 1882 (1908); Bishop Tingle and Brenton, *Ibid.*, **31**, 1157 (1909); Bishop Tingle and Bates, *Ibid.*, **31**, 1233 (1909); Bishop Tingle and Brenton, *Ibid.*, **32**, 113 (1910).

In the case of the phthalamidic acids the particular course which the reaction takes, or the preponderating organic product, if more than one is formed, is determined essentially by the nature of the groups R, R′, R″ which are linked to the nitrogen atoms of the amine or amidic group.

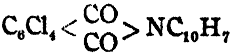
In the present paper we describe the results which we have obtained in the course of an investigation of phthalamidic acids containing one or more chlorine atoms or nitro groups in the benzene nucleus. In this connection we have investigated a number of amidic acids derived from 3,6-dichloro-, tetrachloro-, 3-nitro- and 4-nitrophthalic acids.

We have isolated *di-m-toluidine* and *di-p-chloroaniline 3,6-dichlorophthalates* and have materially improved Graebe's method for the preparation of 3,6-dichlorophthalophenylamidic acid, $C_6H_5NHCOC_6H_2Cl_2CO_2H$, and of its anil. Our products appear to be superior in purity to those described hitherto.

Unlike other members of this series, 3,6-dichlorophthalophenylamidic acid does not appear to be dehydrated by the action of amines in solution, but it is very readily transformed into the anil  $Cl_2C_6H_2<\genfrac{}{}{0pt}{}{CO}{CO}>NC_6H_5$, by the action of 50 per cent. alcohol. It furnishes, therefore, another example of the marked dehydrating power of even dilute alcohol. This phenomenon was discussed in an earlier paper by Bishop Tingle and Rolker.[2]

Entirely similar transformation results were observed with *tetrachlorophthalophenylamidic acid*, $C_6H_5NHCOC_6Cl_4CO_2H$. This acid is prepared most conveniently from tetrachlorophthalic anhydride and aniline, in benzene solution, but it may also be obtained by hydrolysis of the phenylimide. Its *sodium* and *potassium salts* form colloidal solutions in water; when these liquids are shaken, well-marked lathers are produced.

o-Toluidine and tetrachlorophthalic acid or its anhydride give what is, apparently, *tetrachlorophthalo-o-tolylamidic acid*, $CH_3C_6H_4NHCOC_6Cl_4CO_2H$; it is deposited in lustrous, white crystals, melting at 218–20°.

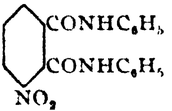
For comparison with the above phenylamidic acid we prepared *tetrachlorophthalo-β-naphthylamidic acid*, $C_{10}H_7NHCOC_6Cl_4CO_2H$, and the corresponding *β-naphthylimide*,  $C_6Cl_4<\genfrac{}{}{0pt}{}{CO}{CO}>NC_{10}H_7$. Both of these compounds are white, crystalline substances, melting at 287°, *i. e.*, the melting point of the imide. The β-naphthylamidic acid resembles the phenyl derivative in general properties, but it is somewhat less stable and is hydrolyzed by alkalies to its constituents with relative ease. Its transformation into the β-naphthylimide does not appear to be influenced by the presence of amines.

---

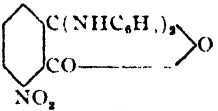
[1] Bishop Tingle and Bates, *loc. cit.*

[2] THIS JOURNAL, 30, 1884 (1908).

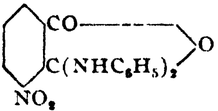
3-Nitrophthalophenylamidic acid, $C_6H_5NHCOC_6H_3(NO_2)CO_2H$, was prepared from the phenylimide.[1] When heated at about 100°, with alcohol (50%), it is changed slowly to a 3-nitrophthalodianilide, which is also formed, under similar conditions, in the presence of amines such as aniline, quinoline or *p*-toluidine. Our dianilide melted at 233–4° and is evidently isomeric with that of Chambers,[2] which melts at 211–2°. Chambers did not determine the structure of his compound, which was prepared from 3-nitrophthalyl chloride, but he pointed out that, according to theory, there should be three dianilides of 3-nitrophthalic acid, *viz.*



I.



II.



III.

On account of its method of formation and of its higher melting point, our compound is probably the symmetrical derivative (I).

In this connection it is interesting to point out the effect of the nitro group in determining the production of the *dianilide* as the only product of the reaction. In the case of the compounds studied hitherto, the chief product has always been an imide, $C_6H_mX_n<\genfrac{}{}{0pt}{}{CO}{CO}>NR$ (X = H or Cl), a dianilide, if formed at all, being obtained only in very small quantity.

4-Nitrophthalophenylamidic acid, $C_6H_5NHCOC_6H_3(NO_2)CO_2H$, was prepared from the phenylimide obtained by Graebe and Buenzod,[3] or, more conveniently, by the action of aniline on 4-nitrophthalic anhydride. For the hydrolysis of the phenylimide Bogert[4] used baryta water; we find that an aqueous solution of potassium hydroxide is much more desirable. Our acid melted at 192°, not 181° as stated by Bogert, and, contrary to his experience, it dissolved without difficulty in a cold, aqueous solution of sodium carbonate. Our specimens of the phenylimide melted at 200–1°; Bogert[5] found 194°.

It is, perhaps, worth mentioning that the amidic acids, with which the senior author has worked during the past few years, frequently melt at temperatures about 15–20° lower than the melting points of the corresponding substituted imides, they then solidify and remelt at a higher temperature. It is found, however, that preparations which behave in this manner are almost always slightly impure. After further treatment they show the same melting point as the substituted imide and this temperature is always a degree or two higher than the second melting point mentioned above. It is, perhaps, hardly necessary to remark that, in every experiment which we have described, precautions have been taken in order to demonstrate that the final methods of purification which were adopted did not themselves convert the acids into their imides.

---

[1] *Ber.*, 32, 1992.

[2] This Journal, 25, 611.

[3] *Ber.*, 32, 1993.

[4] This Journal, 23, 740.

[5] *Ibid.*, 23, 757.

When heated on a boiling water bath, during 5 hours, with alcohol (50 per cent.), with and without the addition of quinoline, 4-nitrophthalophenylamidic acid is transformed, in part, into the phenylimide, the remaining acid being recovered unchanged. Under similar conditions, with alcohol (50 per cent.) and aniline, the same products are obtained, together with a small quantity of a *compound*, melting at 199–200°. In view of the results observed with the 3-nitro acid (see above) and from the fact that the new compound is not attacked by boiling with aqueous solutions of potassium hydroxide, or of hydrochloric acid, we conclude that the substance in question is probably *4-nitrophthalodianilide*, $O_2NC_6H_3(CONHC_6H_5)_2$.

A comparison of the results of the transformation experiments with 3-nitrophthalophenylamidic acid and those of the 4-nitro acid show that the approximation of negative groups [$CO_2H : CO_2H : NO_2 = 1 : 2 : 3$] inhibits the formation of the phenylimide and greatly favors that of the dianilide. The opposite result is obtained when the nitro group is in the 4-position. It is, of course, easy to ascribe this inhibition of the imide formation to "steric hindrance," but we prefer to regard it as being due to a specific influence of the nitro group. The chief ground for this attitude is the fact that the 3,6-dichloro- and the tetrachlorophthalophenylamidic acids form phenylimides readily, although they show a specific insensibility to the transforming influence of amines.

4-Nitrophthalo-β-naphthylamidic acid, $C_{10}H_7NHCOC_6H_3(NO_2)CO_2H$, is prepared by mixing acetone or benzene solutions of β-naphthylamine and 4-nitrophthalic anhydride. After purification the acid is deposited in light yellow crystals, melting at 202–4°.

Camphorphenylamidic acid, $C_6H_5NHCOC_8H_{14}CO_2H$, was prepared by the method of Auwers and Schleicher,[1] from aniline and camphoric anhydride. *Camphor-β-naphthylamidic acid*, $C_{10}H_7NHCOC_8H_{14}CO_2H$, was obtained in a similar manner from β-naphthylamine. It is crystalline and melts at 220–1°. Neither of these acids was changed by prolonged heating at the temperature of a boiling water bath, in presence of alcohol (50 per cent.), or of various amines.

---

[1] *Ann.*, 309, 341.

In our earlier paper[1] we called attention to the readiness with which amidic acids of the phthalic series formed imides, $R<{CO \atop CO}>NX$ (and other compounds), as compared with the stability in this respect of the analogous acids of the aliphatic series. Expressed in another way, the question is one of the relative stability of the substituted ammonium salts of the acids of the two series. After discussing the matter briefly, we reached the conclusion that the instability of the ammonium phthalamidates can be due only "to the inherent properties of the benzene nucleus," whatever this may mean.

Our object in preparing camphorphenyl- and β-naphthylamidic acids was to obtain further light on this point. They are the most readily available derivatives of the alicyclic series and, as stated above, their behavior is essentially similar to that of the corresponding aliphatic compounds. Consequently our previous conclusion, regarding the effect of the benzene nucleus, is still valid, but it may be supplemented by the statement that the accumulation and approximation of negative groups in the phthalic acid nucleus favors the formation of dianilides, $C_6XY(CONHC_6H_5)_2$, rather than that of imides, $C_6XY<{CO \atop CO}>NR$.

Experimental.

1. DERIVATIVES OF 3,6-DICHLOROPHTHALIC ACID.—The following salts have been prepared. *Di-m-toluidine 3,6-dichlorophthalate*, $Cl_2C_6H_2(CO_2NH_3C_6H_4CH_3)_2$, is obtained as a light colored precipitate by mixing the acid and amine in concentrated, alcoholic solution. It is deposited, after recrystallization from water or alcohol, in light yellow crystals, melting at 176°. Found: N, 6.68; calculated, 6.28 per cent. *Di-p-chloroaniline 3,6-dichlorophthalate*, $Cl_2C_6H_2(CO_2NH_3C_6H_4Cl)_2$, is prepared in a similar manner from *p*-chloroaniline and 3,6-dichlorophthalic acid, in benzene solution. Light yellow crystals from water or alcohol, melting at 215°. Found: N, 5.90; calculated, 5.70 per cent.

Only tarry products were obtained by heating 3,6-dichlorophthalic acid with aniline or acetanilide, under various conditions of temperature, with and without solvents.

3,6-Dichlorophthalic anhydride was most easily prepared by heating the acid, at 40°, in a current of dry air, until water ceased to be evolved. The purification of the product is somewhat tedious. We found it best to dissolve the material in benzene and add a little gasoline. After a few hours a resinous deposit is formed on the sides of the container. The clear liquid is decanted and a little more gasoline added and the process repeated until no more resin is precipitated. To the clear liquid three or four volumes of gasoline are now added, whereupon the anhydride will be precipitated as a white powder. In order to purify it completely it may be necessary to dissolve it in a little benzene, at the ordinary temperature, and repeat the treatment with gasoline.

---

[1] THIS JOURNAL, 31, 1235.

Preparation of 3,6-dichlorophthalanil and of 3,6-dichlorophthalophenylamidic acid.—We made numerous attempts to prepare these compounds by Graebe's method,[1] which consists in heating aniline 3,6-dichlorophthalate. We varied the conditions rather widely, but at the best the yield of crude product was very poor and a great deal of it was lost because it was necessary to recrystallize it several times from acetic acid and to boil it with bone-black in order to obtain it in a condition of approximate purity. The small quantity of material which we obtained ultimately was hydrolyzed by means of an aqueous solution of potassium hydroxide. After acidification with hydrochloric acid a brownish precipitate was deposited; it was identified as 3,6-dichlorophthalophenylamidic acid by means of a mixed melting point.

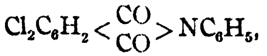
Having found that Graebe's method was entirely unsuited for the preparation of the amidic acid, except in minute quantities, we devised the following process by which the acid may be obtained in a quantitative yield. Aniline (2 mols.) is added to 3,6-dichlorophthalic anhydride (1 mol.), dissolved in benzene. Water and potassium hydroxide (1 mol.) are then added and the mixture is boiled for some time and well stirred. After cooling, the benzene, which contains the excess of the aniline, is removed and the aqueous solution is acidified by means of hydrochloric acid. The resulting precipitate is light brown; this color appears to be due to the presence of a little impurity which is derived from the anhydride and which lowers the melting point of the amidic acid considerably. In order to remove this colored substance it was necessary to dissolve the crude acid in an aqueous solution of sodium hydrogen carbonate; this solution was boiled with bone-black, the acid reprecipitated and recrystallized twice from alcohol and twice from a mixture of benzene and gasoline. The 3,6-dichlorophthalophenylamidic acid, $C_6H_5NHCOC_6H_2Cl_2CO_2H$, which was ultimately obtained, was a light brown powder, melting at 165°. It dissolves readily in benzene, acetone, ether, alcohol, ethyl acetate and in a cold, aqueous solution of sodium carbonate. Found: Cl, 22.99; calculated, 22.90 per cent.

Transformations of 3,6-Dichlorophthalophenylamidic Acid.—The acid was not changed by dissolving it in benzene and heating the solution on a boiling water bath. The addition of aniline, quinoline, or β-naphthylamine produced no effect.

With 50 per cent. alcohol, instead of benzene, a part of the acid is transformed into the anil. The heating was continued during 35 minutes. The presence of aniline, quinoline, or β-naphthylamine does not appear to influence either the velocity or extent of this dehydration. These facts are discussed in the theoretical part of the present paper; they are of considerable interest in connection with the earlier work of Bishop Tingle and Rolker.[1]

---

[1] *Ber.*, **33**, 2019 (1900).

We have found that 3,6-dichlorophthalanil,  $Cl_2C_6H_2<\substack{CO \\ CO}>NC_6H_5$, is most conveniently prepared, in the manner described above, by heating the amidic acid with alcohol. The product melts at 201°. Graebe's material, obtained by fusing the aniline salt, was evidently impure. It is stated to melt at 191°.

EXPERIMENTS WITH TETRACHLOROPHTHALIC ACID. *o-Toluidine and Tetrachlorophthalic Acid.*—*o*-Toluidine (2 mol.) and the acid or anhydride were mixed in acetone solution. The precipitate which forms immediately was purified by solution in water or ethyl acetate, from either of which it is deposited in lustrous white crystals. It melts at 218–20° and is probably tetrachlorophthalo-*o*-tolylamidic acid, $CH_3C_6H_4NHCOC_6Cl_4CO_2H$. Found: N, 3.95; calculated, 3.56 per cent.

Preparation of Tetrachlorophthalophenylimide and of Tetrachlorophthalophenylamidic Acid.—The phenylimide was prepared by Graebe and Buenzod's method, which consists in the fusion of aniline tetrachlorophthalate.[2] The yield is quite poor and it is difficult to purify the product.

Tetrachlorophthalophenylamidic acid, $C_6H_5NHCOC_6Cl_4CO_2H$, may be obtained by boiling the anil, during 2–3 hours, with a rather concentrated aqueous solution of potassium hydroxide, but it is prepared much more easily by adding aniline to tetrachlorophthalic anhydride, both in benzene solution. The precipitate which forms immediately is collected and is purified by dissolving it in a warm, aqueous solution of sodium carbonate and subsequently adding hydrochloric acid. It is readily soluble in acetone, ether, or ethyl acetate and is deposited from alcohol in white crystals, melting at 266°, *i. e.*, at the same temperature as the anil. Specimens which have been insufficiently purified melt about 230°, then become solid and finally remelt a little below 266°. Found: N, 3.76; calculated, 3.69 per cent.

In aqueous solution the acid reddens litmus paper immediately and it dissolves without difficulty in warm, aqueous solutions of alkali hydroxides, but cold solutions attack it only slowly because its *sodium* and *potassium salts* are colloidal and soapy and readily form lathers. When a warm aqueous solution of either of these salts is cooled it becomes turbid, then jelly-like and finally, if the liquid is sufficiently concentrated, a tarry or resinous precipitate is formed.

[1] *Loc. cit.*

[2] *Ber.*, 32, 1994.

Transformations of Tetrachlorophthalophenylamidic Acid.—The acid was recovered unchanged after boiling during 35 minutes in benzene solution. The addition of aniline was without effect. In 50 per cent. alcohol, on a boiling water bath, a part of the acid is transformed into the anil. The reaction does not appear to be influenced by the presence of aniline, or of β-naphthylamine.

On account of their identical melting points, as mentioned above, some trouble was at first encountered in distinguishing between tetrachlorophthalophenylamidic acid and the phenylimide; this difficulty is increased by the fact that the acid does not dissolve easily in a cold, aqueous solution of potassium hydroxide. The most ready methods of identification were the solubility of the acid in a boiling, aqueous solution of sodium carbonate and the fact that the aqueous solution of the acid reddens litmus paper. Tetrachlorophthalophenylamidic acid changes slowly to the phenylimide at the ordinary temperature, consequently the material employed for the transformation experiments described above was carefully purified by means of sodium carbonate solution immediately before use.

Tetrachlorophthalo-β-naphthylamidic Acid.—This acid, $C_{10}H_7NHCOC_6Cl_4CO_2H$, is prepared from β-naphthylamine and tetrachlorophthalic anhydride, in a simliar manner to the phenyl derivative. The *sodium* and *potassium salts* dissolve with difficulty in water, at the ordinary temperature and the resulting solutions are colloidal, consequently it is somewhat troublesome to separate the amidic acid from unchanged β-naphthylamine. The best plan we found was to add dilute hydrochloric acid to a boiling aqueous solution of the sodium salt, collect the precipitated acid and boil it with a large quantity of water; after drying it is treated with a mixture of toluene and glacial acetic acid; from this it deposits in white crystals, melting at 287°, which is the m. p. of the β-naphthylimide. It dissolves readily in ethyl acetate, acetone and in 95 per cent. alcohol, is less soluble in ether, chloroform and in 50 per cent. alcohol and is practically insoluble in benzene. Found: N, 3.23; calculated, 3.26 per cent.

The acid changes slowly, at the ordinary temperature, to the β-naphthylimide. Concentrated, aqueous potassium hydroxide solution hydrolyzes it slowly to β-naphthylamine and tetrachlorophthalic acid, both of which were fully identified.

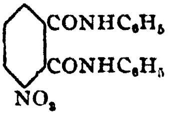
Highly purified tetrachlorophthalo-β-naphthylamidic acid is transformed into the β-naphthylimide when heated with alcohol of 95 or 50 per cent. The change was not complete during the time of our experiments, about 35 minutes, and the reaction does not appear to be influenced by the addition of aniline or β-naphthylamine to the alcoholic solution.

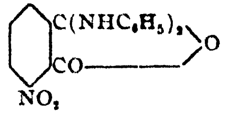
Tetrachlorophthalo-β-naphthalo-β-naphthylimide, $C_6Cl_4 < \begin{matrix}CO\\CO\end{matrix} > NC_{10}H_7$, is prepared by heating the acid at 260–70°, during 10 minutes. It is soluble in acetone, ethyl acetate, or alcohol and is deposited in white crystals, melting at 287°. The compound does not dissolve in an aqueous solution of sodium carbonate, but by the action of a warm, aqueous solution of potassium hydroxide it is hydrolyzed slowly to potassium tetrachlorophthalo-β-naphthylamidate, which, of course, goes into solution.

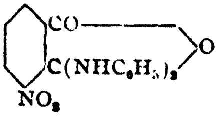
DERIVATIVES OF 3-NITROPHTHALIC ACID.—3-Nitrophthalophenylamidic acid, $C_6H_5NHCOC_6H_3(NO_2)CO_2H$, was prepared by the hydrolysis of the phenylimide. We found that this was readily accomplished by warming with an aqueous solution of potassium hydroxide, in place of the barium hydroxide employed by Bogert.[1] After several recrystallizations from ethyl acetate our material melted at 181° and, contrary to the statement of Bogert,[2] dissolved readily in an aqueous solution of sodium carbonate, at the ordinary temperature.

Transformation of 3-Nitrophthalophenylamidic Acid.—At the temperature of a boiling water bath, during 35 minutes, the acid is not changed in presence of alcohol (50 per cent.), or of quinoline, but on adding aniline to the alcohol a little 3-nitrophthalodianilide is produced and the yield of this compound is quantitative if the heating is prolonged during 5 hours. With *p*-toluidine or alcohol (50 per cent.), during 5 hours' heating, the acid also gives a small quantity of the same dianilide. This *dianilide* was obtained in crystals, melting at 233–4°. It is readily soluble in alcohol, chloroform, ether, acetone, or ethyl acetate, but dissolves with difficulty in benzene, or toluene. The compound is not attacked by a boiling, aqueous solution of potassium hydroxide, nor by hydrochloric acid. Found: C, 66.76; H, 4.66. Calculated: C, 66.48; H, 4.15 per cent.

Our 3-nitrophthalodianilide appears to be isomeric with one prepared by Chambers[3] from 3-nitrophthalyl chloride. It is uncertain which of the three possible structures







are to be assigned to the two compounds in question, but we think that ours is probably the symmetrical derivative.

3-Nitrophthalic Anhydride and β-Naphthylamine.—When these substances are mixed in an organic solvent, a compound is precipitated which appears to be *3-nitrophthalo-β-naphthylamidic acid*, $C_{10}H_7NHCOC_6H_3(NO_2)CO_2H$. Its purification is attended with considerable difficulty on account of the progressive formation of an oily material. We obtained light yellow crystals from a mixture of acetone, benzene and chloroform; they melted at 201–2° and dissolved easily in alcohol, ethyl acetate, acetone, or ether, less readily in chloroform. That the compound is an acid is shown by the fact that it is soluble in an aqueous solution of sodium carbonate and is reprecipitated on acidification with hydrochloric acid. The quantity of purified material ultimately available was too small to permit of analysis.

---

[1] THIS JOURNAL, 23, 740.

[2] *Loc. cit.*

[3] THIS JOURNAL, 25, 611.

DERIVATIVES OF 4-NITROPHTHALIC ACID.—4-Nitrophthalophenylamidic acid, $C_6H_5NHCOC_6H_3(NO_2)CO_2H$, was obtained from the phenylimide, which was prepared by Graebe and Buenzod's method.[1] This consists in heating aniline 4-nitrophthalate. The resulting anil, after purification, was dissolved in a warm, aqueous solution of potassium hydroxide, the heating continued during about 5 minutes and the amidic acid precipitated by means of dilute hydrochloric acid. The acid was then crystallized several times from ethyl acetate, in order to separate it from tarry matter which is always produced during the fusion of the aniline 4-nitrophthalate.

The phenylamidic acid may also be obtained by mixing benzene solutions of aniline and 4-nitrophthalic anhydride. The product obtained in this manner is less difficult to purify than that prepared from the anil. The acid was dissolved in a cold, aqueous solution of sodium carbonate, reprecipitated by means of dilute hydrochloric acid and recrystallized several times from ethyl acetate. Our acid melted at 192°. The method of preparation given above is much more convenient than that described by Bogert.[1] He hydrolyzed the anil by the use of barium hydroxide, added sulphuric acid and extracted the amidic acid by means of alcohol. His product melted at 181°, and did "not appear to decompose carbonates." Our material dissolved in a cold, aqueous solution of sodium carbonate after 10–15 minutes. Bogert gives 194° as the m. p. of 4-nitrophthalophenylimide.[2] Our preparation melted at 200–1°.

We refer, in the first part of this paper, to a peculiarity shown by the acids of this series in regard to their melting points.

Transformation of 4-Nitrophthalophenylamidic Acid.—At the temperature of a boiling water bath, after 5 hours, in presence of alcohol (50 per cent.), a part of the acid was recovered unchanged, the remainder being converted into the phenylimide. A similar result was obtained by adding quinoline to the solution. After 6 hours' heating, under similar conditions, with a mixture of alcohol (50 per cent.) and aniline, the products consisted of unchanged acid, phenylimide and a *compound,* melting at 199–200°. It was not attacked by boiling with aqueous solutions of potassium hydroxide, or hydrochloric acid; boiling with alcoholic solutions of the same reagents produced only a slight effect. These results lead to the conclusion that the substance is probably *4-nitrophthalodianilide,* $O_2NC_6H_3(CONHC_6H_5)_2$, which does not appear to have been described hitherto. The material available was insufficient for an analysis.

---

[1] *Loc. cit.*

[2] *Ibid.*, p. 757.

Preparation of 4-Nitrophthalo-β-naphthylamidic Acid.—This acid, $C_{10}H_7NHCOC_6H_3(NO_2)CO_2H$, was prepared by adding β-naphthylamine to 4-nitrophthalic anhydride, both substances being dissolved in acetone, or benzene. The precipitate which is formed is collected, dried, dissolved in an aqueous solution of potassium hydroxide, the liquid acidified with hydrochloric acid and the precipitated solid recrystallized several times from a mixture of acetone and benzene. In this manner we obtained the acid in light yellow crystals, melting at 202–4°. It dissolves in a cold, aqueous solution of sodium carbonate and is reprecipitated by hydrochloric acid. The acid is readily soluble in acetone, ethyl acetate, alcohol, or ether, less readily in chloroform and practically insoluble in benzene. Found: N, 8.21, calculated, 8.33 per cent.

DERIVATIVES OF CAMPHORIC ACID.—Camphorphenylamidic acid, $C_6H_5NHCOC_8H_{14}CO_2H$, was prepared without difficulty by the method of Auwers and Schleicher;[1] it consists in boiling camphoric anhydride, aniline and chloroform during 3 hours. The product was recrystallized from alcohol.

Camphor-β-naphthylamidic acid, $C_{10}H_7NHCOC_8H_{14}CO_2H$, was prepared in a similar manner to the phenyl derivative, except that the heating was continued during 5 hours. The chloroform was then evaporated, the residue dissolved in a warm, aqueous solution of sodium bicarbonate and the amidic acid precipitated from the clear solution by means of hydrochloric acid. After solution in alcohol the compound was obtained in white crystals, melting at 220–1°. Found: N, 4.39; calculated, 4.30 per cent.

The acid dissolves readily in acetone, alcohol, ethyl acetate, chloroform, or ether; it is slightly soluble in benzene and in hot water. In solution the acid reddens blue litmus paper and it dissolves in a warm, aqueous solution of sodium carbonate. The *sodium* and *potassium salts* are somewhat colloidal and soapy.

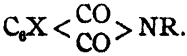
Neither camphorphenyl- nor β-naphthylamidic acids could be transformed into the imides at the temperature of a boiling water bath. The experiments were made in alcoholic solution (50 per cent.), the heating continuing during 35 minutes in the case of the phenyl compound and

---

[1] *Ann.*, 309, 341.

6 hours in that of the β-naphthyl derivative. The addition of aniline or quinoline to the alcoholic solution of the phenylamidic acid and of β-naphthylamine to that of the β-naphthylamidic acid produced no effect. It is clear, therefore, that these two acids resemble the aliphatic amidic acids and differ from those of the aromatic series.

Summary.

1. We have prepared a number of phthalamidic acids of the type $RNHCOC_6XCO_2H$, where R = phenyl or β-naphthyl and X represents H_2Cl_2, Cl_4 or H_3NO_2.
2. The behavior of these acids when heated with alcohol alone and also with alcohol and amines has been studied.
3. The accumulation and approximation of negative groups in the phthalic acid nucleus favors the formation of diamides, $C_6X(CONHR)_2$, rather than that of imides,  $C_6X<\genfrac{}{}{0pt}{}{CO}{CO}>NR$.
4. Camphoramidic acids, $RNHCOC_8H_{14}CO_2H$, ($R = C_6H_5$ or β-naphthyl) resemble the corresponding aliphatic acids and not those of the aromatic series. They are stable under the conditions employed.
5. A number of new compounds are described, and improved methods have been worked out for the preparation and purification of certain substances which had been obtained previously by other chemists.

The investigation is being continued in various directions.

McMaster University,
Toronto, Canada.

THE BASIC PROPERTIES OF OXYGEN: COMPOUNDS WITH BROMINE AND IODINE.

By D. McIntosh.

Received August 5, 1910.

Two addition compounds of ether and bromine are known. One, which we may call the tribromide (m. p. 22°)[1] consists of three, and the other, the dibromide (m. p. —40°)[2], of two atoms of bromine to a molecule of ether.

The constitution of the dibromide may be explained in several ways, assuming the oxygen to be quadrivalent and the bromine uni- or trivalent. The tribromide, however, can be conveniently expressed only by doubling the formula and writing it $C_4H_{10}O = Br - Br = Br - Br = Br - Br = OH_{10}C_4$; and as nothing is known against this mode of representing the dibromide, either in regard to its molecular weight or its reactions, its formula, too, may be doubled, $(C_4H_{10}O = Br - Br = Br - Br = OH_{10}C_4)$.

---

[1] Schützenberger, *Ann.*, 167, 86 (1873).

[2] *Trans. Chem. Soc.* (London) 87, 784 (1905).

In a recent paper Chelintzev and Kepovalov[1] criticize these formulas and attempt to show that the dibromide has the constitution $C_4H_{10}O\langle^{Br}_{Br}$. As I have tried to determine the molecular weights of these and similar compounds, a brief account of the work may be useful; and while it has been found impossible to decide on the correct formulas it can at least be shown that Chelintzev and Kepovalov misinterpret the results of their experiments.

These investigators prepare what they believe to be the dibromide ether complex by adding absolute ether to pure bromine. After the reaction is complete, the excess of ether is removed by heating to 30° under reduced pressure. They obtain an oily orange-red liquid, etc.

Under such conditions the dibromide is not formed but a mixture of substitution products colored by bromine is produced as repeated analyses have shown. The dibromide can be prepared only with the greatest care at a low temperature. Then it may be obtained with less than $^1/_{20}$ per cent. hydrobromic acid. Above its melting point (—40°) substitution takes place, so that a mixture of bromine and ether may contain a large amount of acid.

In parallel columns are placed the properties given to the compound by Chelintzev and his collaborator and those of the pure dibromide.

Chelintzev and Kepovalov	McIntosh
Orange-red liquid.	Bromine colored liquid.
Soluble in benzine, benzene and carbon disulphide on warming, precipitated on cooling.	Decomposed
Soluble in chloroform.	Largely decomposed.
Partly soluble in carbon tetrachloride.	" "
Soluble in ethyl alcohol and ethyl acetate with heat evolution.	" "
Changed slowly by KOH solution.	Instantly decomposed.
Acid fumes evolved in strong sulphuric acid.	" "
Little affected by sodium acid sulphite solution.	" "
Slowly acts on potassium iodide solution.	Instant decomposition with liberation of iodine
Heat of formation 9130 cal.	Under 2000 cal.

These investigators find the molecular weight of their compound in acetic acid by the cryoscopic method to be about 240. The dibromide, however, is decomposed by this solvent and its molecular weight cannot be determined.

Freezing-point measurements of this substance were made with chloroform (m. p. —63°) as solvent. The compound was partly decomposed, and the freezing-point lowerings, although a little less than the sum of the ether and bromine depressions determined separately, could not be used to fix its molecular weight.

---

[1] *Ber.*, 42, 1531 (1909).

An attempt was made to determine the molecular weight of these bromides by Ramsay and Shields' method. The figures for the tribromide[1] may be given:

FORMULA TAKEN FOR CALCULATION $C_4H_{10}OBr_3$.

T.	$\gamma(MV)^{2/3}$.
25.9	1229.5
29.6	1223.0
37.2	1201.2
45.0	1175.3

When plotted these members lie approximately in a straight line. Between 25° and 45° $\frac{d\gamma(MV)^{2/3}}{dT} = 2.85$ while for normal compounds the value is 2.12. Clearly the compound is largely dissociated. The dibromide separates into two layers 10° above its melting point. It, too, is largely dissociated.

These results show that the ordinary methods of molecular weight determinations are not applicable to these oxonium compounds, and that the formulas must remain in doubt until other methods are devised.

While examining the action of bromine and chlorine on the alcohols, ketones, etc., in 1905, a large amount of time was spent in attempting to produce analogous compounds with iodine. Quite recently Waentig[2] has made some experiments on this point and believes that he has obtained addition products at low temperatures.

When a solution of iodine in alcohol or acetone is cooled to —80° or —90° the iodine may separate and be mistaken for a compound, but when carefully dried at a low temperature analyses show the product to be iodine contaminated with a little of the organic solvent. With ethyl acetate mixed crystals of the solvent and iodine may be obtained.

Bromine and chlorine when dissolved in organic substances containing oxygen give a noticeable heat evolution; iodine a slight heat absorption.

If iodine gives compounds analogous to those formed by the other halogens, the reaction between iodine and ether may be represented by the equation

$$\overset{\text{A.}}{C_4H_{10}O + I_2} \rightleftarrows \overset{\text{B.}}{C_4H_{10}OI_2}$$

or $K = B/A$, where K is the equilibrium constant, and B and A the concentrations of the substances involved.

---

[1] The tribromide always contains several per cent. hydrobromic acid.

[2] *Z. physik. Chem.*, 68, 1513 (1909).

From van't Hoff's equation

$$\log K_2 - \log K_1 = \frac{q}{2}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Where K_1 and K_2 are the equilibrium constants at the temperatures T_1 and T_2, T_2 being the higher, and q the heat of formation of A. Since q is positive[1] K_2 must be larger than K_1 or less of the compound is produced at a low temperature than at a higher one. It seems probable, then, that these compounds cannot be produced in a reasonably pure state by cooling their solutions to a low temperature.

McGill University.

[Contribution from the Chemical Laboratory, University of Illinois.]

MOLECULAR REARRANGEMENTS OF CARBON COMPOUNDS.[2]

By C. G. Derick.

Received July 12, 1910

Table of Contents.

1 Types of Chemical Reaction 2. Formation and Stability of Compounds that Rearrange. 3. Catalysis of Speed of True Rearrangements of the Non-reversible Type. 4 A Correlation of True Molecular Rearrangements of Acids and Bases, Belonging to the Non-reversible Type, with the Free Energy of Ionization 5. Rearrangements of Unsaturated Acids 6 Illustrations of True Rearrangements of Non-reversible Type 7. Rearrangements with Reaction 8 Review of the Field of Molecular Rearrangements

1. Types of Chemical Reaction.

In the study of molecular rearrangements of carbon compounds, two types of chemical reactions are noted; the reversible and non-reversible.[3] Tautomerism furnishes many examples of molecular rearrangements of the reversible type. Wislicenus showed, in the case of formylphenylacetic ester,[4] that in certain solvents an equilibrium between the two isomeric forms is established, which equilibrium is dependent upon temperature, concentration, and the nature of the solvent. Molecular rearrangements of the non-reversible type are illustrated by the change of Δ^2 unsaturated acids into their Δ^1 isomers by boiling with alkalis.

A further study of reversible and non-reversible molecular rearrangements shows that certain rearrangements occur when atoms are added to or substracted from the original molecule, while in many other cases the rearrangement consists only in the readjustment of the atoms already present in the molecule. Molecular rearrangements of the former class will be termed rearrangements with reaction while those of the latter class will be called true rearrangements or rearrangements without reaction. Tautomeric changes illustrate true rearrangements of the reversible type, while the change of Δ^2 unsaturated acids to their Δ^1 isomers furnish illustrations of non-reversible rearrangements of this class. The historic rearrangement of pinacone to pinacolin by the elimination of water illustrates a rearrangement with reaction. The following discussion will deal mainly with true rearrangements of the non-reversible type.

---

[1] Contrast Hildebrand and Glascock, This Journal, 31, 26 (1909).

[2] Presented in abstract at the Boston meeting of the American Chemical Society. From the author's thesis in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

[3] For a definition of these terms see Nernst, Theoretische Chemie, Sechste Auflage, especially pages 668–70.

[4] Wislicenus, *Ann.*, 306, 322 (1899); 300, 206.

2. Formation and Stability of Compounds that Rearrange.

It has often been suggested by chemists that molecular rearrangements occur in the direction to produce a more stable substance. Before this idea can be developed it is necessary to consider carefully the conditions under which compounds rearrange, as well as the nature of the compounds. Nernst[1] states: "The fact that reaction velocity in chemical systems is usually extraordinarily small, no matter how far removed from the point of equilibrium, is of the very greatest importance for our knowledge of chemical compounds. Probably nine-tenths, or rather ninety-nine one hundredths, of all organic compounds would never have seen the light of day if they had proceeded to their stable conditions with greater velocity. The many polymeric hydrocarbons of the formula C_nH_n could not exist at the same time if they all tended to go at once to the system of greatest stability corresponding to the formula C_nH_n. In the sense of the preceding, *organic chemistry is peculiarly the region of unstable compounds*, and these either go over to a more stable form very slowly in a measurable time or else not at all. In most cases heat only accelerates a reaction—whether a decomposition or a union—which would take place spontaneously, though, to be sure, perhaps only during the lapse of, say, a thousand years."

Baeyer, in his work upon terephthalic and phthalic acids, furnishes the experimental part to Nernst's discussion. Terephthalic acid upon reduction in the cold with sodium amalgam, in the presence of carbon dioxide to remove the hydroxyl ion, gives $\Delta^{2,5}$-dihydroterephthalic acid. This acid rearranges to the $\Delta^{1,5}$ isomer upon warming with water. The $\Delta^{1,5}$ acid, when boiled in the presence of hydroxyl ions, gives the $\Delta^{1,4}$-dihydroterephthalic acid. Baeyer concluded that the $\Delta^{2,5}$-dihydro acid is the most unstable, while the $\Delta^{1,4}$ isomer is the most stable. Using a more vigorous reducing agent, namely sodium amalgam in the absence of carbon dioxide gas, he obtained no $\Delta^{2,5}$-dihydroterephthalic acid, but more stable products. On the other hand, the reduction of phthalic acid at a higher temperature by sodium amalgam in the absence of carbon dioxide gives the most stable tetrahydrophthalic acid. No unstable intermediate dihydro or more unstable isomeric tetrahydro acids could be formed under these conditions, so that molecular rearrangements are not possible, because the product first formed by the reduction is the most stable. Thus the conditions under which compounds must be formed which undergo true molecular rearrangements of the non-reversible type, become evident, namely that the reagents used at the time of formation as well as the speed of the reaction must be such that unstable compounds are produced.

---

[1] Nernst, Theoretical Chemistry. Translation of revised 4th German edition, 672.

3. Catalysis of Speed of True Rearrangements of the Non-reversible Type.

According to Nernst the unstable compounds, considered above, may be going over to a more stable state very slowly in a measurable time or else not at all. It is evident that true rearrangements of the non-reversible type occur in unstable compounds which go, spontaneously, to a more stable state. In the case of the rearrangement of $\Delta^{2,5}$-dihydroterephthalic acid to the $\Delta^{1,5}$ isomer, simply heating with water caused the reaction to be complete in a short time. In many other cases heat is the only thing necessary to complete the rearrangement in a short time. The $\Delta^{1,5}$-dihydroterephthalic acid rearranged to the $\Delta^{1,4}$ isomer when boiled with hydroxyl ions. Thus it appears that the reagents used in true rearrangements of the non-reversible type are catalysts to the speed of the rearrangement and in their presence reactions which might take thousands of years are completed in a few minutes. Goldschmidt and Reinders[1] have proved this to be the case for the change of diazoaminobenzene into aminoazobenzene. A thorough study of the catalytic influence of the reagents added to hasten true rearrangements of the non-reversible type will be made in the near future.

4. A Correlation of True Molecular Rearrangements of Acids and Bases, Belonging to the Non-reversible Type, With the Free Energy of Ionization.

Under 2 it was shown that the reaction velocity and stability were of fundamental importance in the study of rearrangements of this type, so that some measure of these factors must be found. Reaction velocity is readily determined by the amount of the substance changed in a given time, but a measure of stability is not so readily obtained. The term stability is frequently used in a vague way. It has an exact meaning only when the conditions are specified, as will be seen in the following: The above quotation from Nernst makes it evident that when a reaction takes place *spontaneously* (or may so take place if sufficient time is given) the initial substance is unstable with respect to the final and hence there is a decrease in free energy during the change. As stated above, in true rearrangements of the non-reversible type, the initial substance is slowly changing into its isomer even in the absence of a catalyzer. Thus the initial substance in such a rearrangement must be unstable with respect to the final substance. Yet, as stated in the quotation from Nernst, the final substance may be unstable with respect to other substances as, for example, to the elements carbon, hydrogen, and oxygen. Hence in the previous discussion stability toward rearrangements is meant whenever the term is used.

---

[1] *Ber.*, 29, 1369, 1899 (1896).

In seeking a criterion of stability in true rearrangements of the non-reversible type, the logarithm of the ionization constant of acids and bases has been chosen. From the second law of thermodynamics, the expression, $A = RTlnK$, is obtained, in which

A is the free energy of ionization,
R is the gas constant,
T is the absolute temperature, and
K is the ionization constant.

The free energy of ionization of acids and bases is "the change in free energy" as expressed by the reaction $HA \rightleftarrows H^+ + A^-$ for acids and $ROH \rightleftarrows R^+ + OH^-$ for bases when the initial and final substances are at unit concentration. Therefore, the above expression gives a measure of the free energy of ionization in terms of the ionization constant and shows that the free energy of ionization is directly proportional to the natural logarithm of the ionization constant. Since that acid is most stable toward ionization which possesses the smallest amount of free energy of ionization, it is evident that when one acid has a smaller ionization constant than another the change in the free energy of ionization is smaller and its stability with respect to ionization is greater. Therefore to determine the relative stabilities of two acids in terms of the free energy of ionization, we need only to compare the logarithms of their ionization constants.

In the following table examples of true rearrangements of the non-reversible type are given. The Briggsian logarithm of the ionization constant of each acid or base that undergoes the rearrangement is given in column 6, and that of the isomer resulting from the rearrangement is given in column 7. From this table it is evident that the free energy of ionization of the initial substance is greater than that of the final substance and that during the rearrangement there has been a decrease in free energy. The final substance is, therefore, more stable toward ionization than the initial substance. As stated above, the final substance in a rearrangement of this type must be the more stable toward rearrangement, so that that acid or base is most stable toward rearrangement which is also most stable toward ionization as Table I shows. Hence, *the final (stable) substance in a series of true rearrangements of the non-reversible type has a smaller ionization constant (or free energy of ionization) and the logarithm of the ionization constant may therefore be taken as a criterion of stability in these rearrangements.*

The meaning of the classes referred to in Table I will be explained in the final section of this article.

TABLE I.

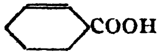
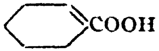
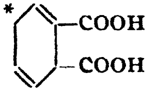
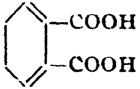
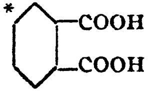
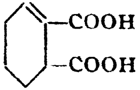
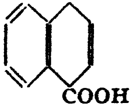
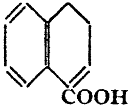
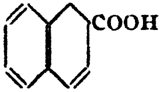
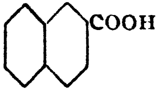
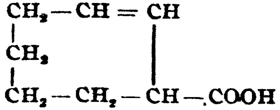
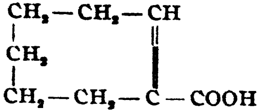
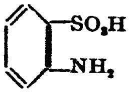
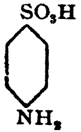
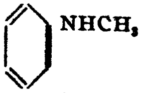
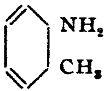
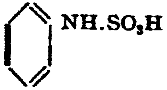
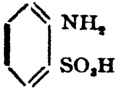
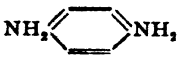
Class.	True molecular rearrangements (non-reversible)		Catalyzer.	Ionization constants at 25°			
				K		Log. $K \times 10^6$.	
	Before.	After.		Before.	After.	Before.	After.
1	$CH_3.CH_2.CH=CH.CH_2COOH$/ Δ^2 Hexenoic acid (Dihydrosorbic acid)	$CH_3.CH_2.CH_2 CH=CH.COOH$ Δ^1 Hexenoic acid	OH^-	2.64×10^{-5}	1.89×10^{-5}	0.423	0.2775
	$CH_3.CH=CH.CH_2COOH$ Δ^2 Pentenoic acid	$CH_3.CH_2.CH=CHCOOH$ Δ^1 Pentenoic acid	OH^-	3.35×10^{-5}	1.48×10^{-5}	0.526	0.172
	 Δ^2 Tetrahydrobenzoic acid	 Δ^1 Tetrahydrobenzoic acid	OH^-	3.05×10^{-5}	2.21×10^{-5}	0.478	0.344
	*  $\Delta^{2,5}$ Dihydrophthalic acid	 $\Delta^{2,6}$ Dihydrophthalic acid	OH^-	2.46×10^{-4}	1.65×10^{-4}	1.392	1.218
2	*  Δ^1 Tetrahydrophthalic acid	 Δ^2 Tetrahydrophthalic acid	OH^-	5.9×10^{-4}	7.6×10^{-5}	1.772	0.882
	 Δ^2 Dihydro-α-naphthylic acid	 Δ^1 Dihydro-α-naphthylic acid	OH^-	1.14×10^{-4}	8.1×10^{-5}	1.058	0.909
	 Δ^2 Dihydro-β-naphthylic acid	 Δ^1 Dihydro-β-naphthylic acid	OH^-	5.9×10^{-5}	2.9×10^{-5}	0.772	0.463

TABLE I—(*Continued.*)

Class.	True molecular rearrangement (non-reversible).		Catalyzer.	Ionization constants at 25°.			
				K.		Log. $K \times 10^5$.	
	Before.	After.		Before.	After.	Before.	After.
	 Δ^2 Cycloheptene carboxylic acid	 Δ^1 Cycloheptene carboxylic acid	OH^-	2.7×10^{-5}	8.3×10^{-6}	$(K \times 10^6)$ 1.433	$(K \times 10^6)$ 0.919
	 Aniline-*o*-sulphonic acid	 Aniline-*p*-sulphonic acid (Sulphanilic acid)	Heat and H_2SO_4	3.3×10^{-3}	5.81×10^{-4}	2 519	1 764
19*	 Methyl aniline	 *o*-Toluidine	Heat	7.4×10^{-9}	1.09×10^{-9}	$(K_b^{100°} + 10)$ 0.869	$(K_b^{100°} \times 10^9)$ 0.038
	 Phenyl sulphamic acid	 Aniline-*o*-sulphonic acid	Heat and H_2SO_4	1.00×10^{-1}	3.3×10^{-3}	4.000	2.518
	$C_6H_5NH.NH_2$ Phenyl hydrazine	 *p*-Phenylene diamine	Heat and HCl	$(K^{40°})$ 1.6×10^{-9}	$(K^{25°})$ 3.1×10^{-10}	(Log. $K \times 10^{10}$) 1.204	(Log. $K \times 10^{10}$) 0.492

* See Section 5.

5. Rearrangements of Unsaturated Acids.

The most thorough test of the principle that true rearrangements of acids or bases of the non-reversible type take place in the direction to decrease the free energy of ionization is that given by the unsaturated acids. Rearrangements of such acids are so common that Thiele's partial valence theory was advanced for the explanation of the reason that $\Delta^{1,3}$ unsaturated acids gave Δ^2 unsaturated acids upon reduction. Further in the literature on unsaturated acids it is constantly noted that Δ^2 unsaturated acids rearrange to the Δ^1 isomer, etc.

Fichter and Pfister[1] first called attention to the fact that the Δ^2 unsaturated acids of the aliphatic series give a greater ionization constant than any of their isomers. The following figures and data will show this principle to be generally true in both open-chain and ring unsaturated acids. In the figures, the ordinates give the Briggsian logarithms of the affinity constants while the abscissas give the positions of the unsaturation in the acids, given in the table following the figures. The logarithm of the affinity constant is used rather than the algebraic value, since the free energy of ionization is proportional to a logarithmic function of the affinity constant and, also, since a comparison of the relative stabilities of the acids toward ionization is desired.

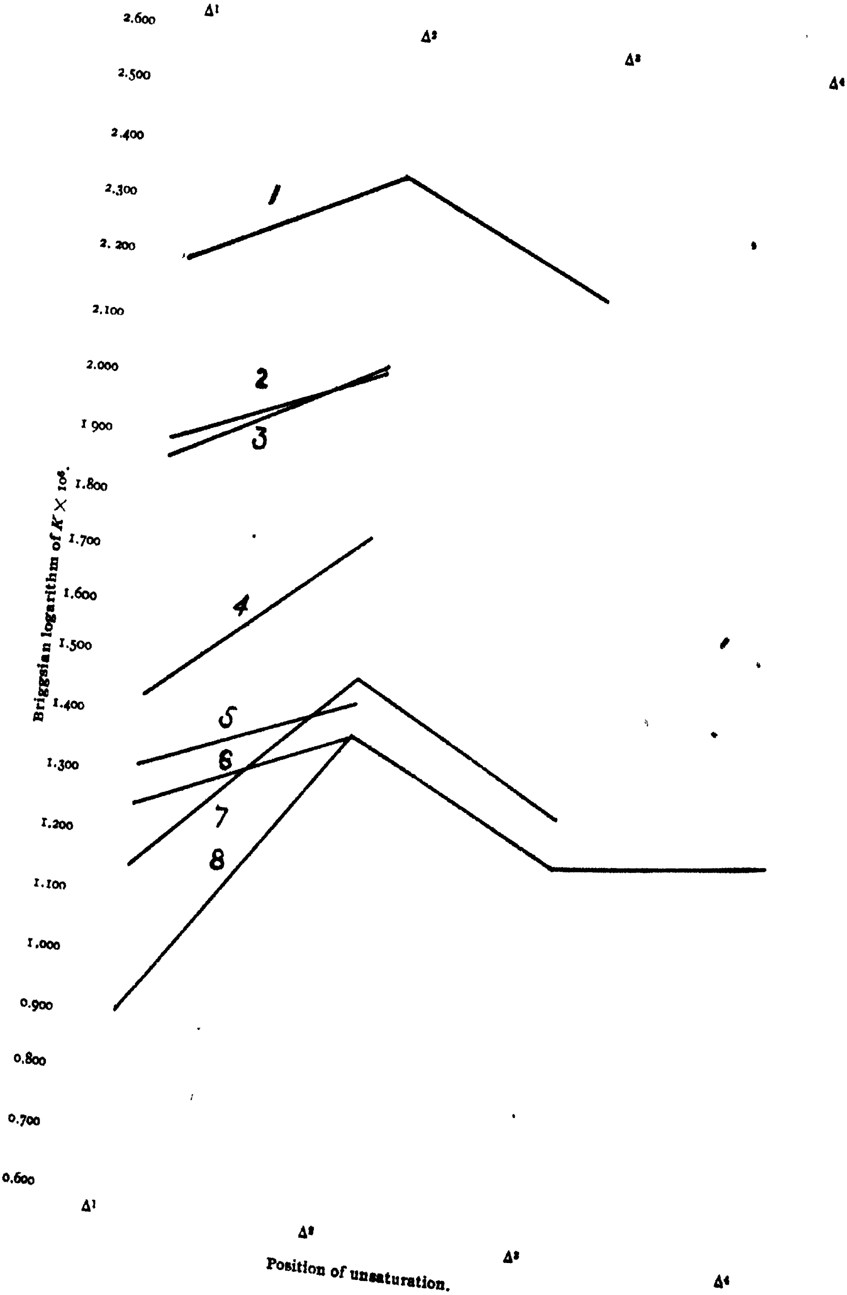
The principle of Fichter and Pfister appears to be general and not a single exception to it is known, while the data given in Table II show that it has been tested for twenty acids. In the case of Δ^1-tetrahydrophthalic acids an apparent exception to this rule is found, which disappears if we start the nomenclature with the other carboxyl so that the Δ^1 and Δ^2* positions are interchanged. The position of the double union then corresponds to that given in the other 18 acids. As Table I shows, these acids all rearrange in the direction to decrease the free energy of ionization so that it may be stated as a general rule *that whenever the unsaturation is Δ^2 with respect to a given carboxyl group true rearrangements of the non-reversible type are possible.*

Thiele and others have found that $\Delta^{1,3}$ unsaturated acids upon reduction give the Δ^2 acids, which, according to the above paragraph, are the most unstable toward ionization of any of their isomers, and rearrangements would be predicted and have been observed quite generally. Nernst states that such unstable isomers are formed under conditions where the speed of reaction at the time of formation is very slight. The above discussion of the reduction of the terephthalic acid showed that when precaution was taken to maintain conditions of slow speed of reaction and to use weak reducing agents the $\Delta^{2,5}$ unsaturated acid resulted.

---

[1] Fichter and Pfister, *Ann.*, 334, 203 (1904).

* See Tables I and II.


Δ¹
Δ²
Δ³
Δ⁴
2.600
2.500
2.400
2.300
2.200
2.100
2.000
1.900
1.800
1.700
1.600
1.500
1.400
1.300
1.200
1.100
1.000
0.900
0.800
0.700
0.600
Briggsian logarithm of K × 10⁶.
1
2
3
4
5
6
7
8
Δ¹
Δ²
Δ³
Δ⁴
Position of unsaturation.

This acid has both double unions Δ^2 to carboxyl groups. It should have the greatest amount of free energy of ionization according to the principle of Fichter and Pfister and should undergo rearrangements, which agrees with the experimental facts as shown above. *Hence it is evident that the compounds from which Thiele deduced his theory of partial valence, as well as other acids which obey the same rule, must be compounds which are formed with weak reducing agents involving small energy changes and where the speed of reaction is small so that compounds result which are very unstable toward ionization, and therefore toward rearrangement.*

TABLE II.- -DATA FOR FIG. 1.

Curve number	Name.	Ionization constant.	
		K.	Log. $K \times 10^6$.
1*	$\Delta^{2,6}$-Dihydrophthalic acid . .	1.65×10^{-4}	2 218
	$\Delta^{2,5}$-Dihydrophthalic acid.	2.46×10^{-4}	2.392
	$\Delta^{2,4}$-Dihydrophthalic acid	1.5×10^{-4}	2.177
2	Δ^1-Dihydro-α-naphthylic acid.	$8\ 1 \times 10^{-5}$	1.909
	Δ^2-Dihydro-α-naphthylic acid	$1\ 14 \times 10^{-4}$	2.058
3*	Δ^2-Tetrahydrophthalic acid. . . .	$7\ 5 \times 10^{-5}$	1 876
	Δ^1-Tetrahydrophthalic acid.	$1\ 18 \times 10^{-4}$	2 0725
4	Δ^1-Dihydro-β-naphthylic acid	2.9×10^{-5}	1 463
	Δ^2-Dihydro-β-naphthylic acid	5.1×10^{-5}	1 772
5	Δ^1-Tetrahydrobenzoic acid . .	2.21×10^{-5}	1 345
	Δ^2-Tetrahydrobenzoic acid	3.05×10^{-5}	1 485
6	Δ^1-Hexenoic acid	$1\ 89 \times 10^{-5}$	1 277
	Δ^2-Hexenoic acid.	$2\ 64 \times 10^{-5}$	1.428—
	Δ^3-Hexenoic acid.	$1\ 74 \times 10^{-5}$	1 241
	Δ^4-Hexenoic acid.	1.91×10^{-5}	1 282
7	Δ^1-Pentenoic acid.	1.48×10^{-5}	1 172
	Δ^2-Pentenoic acid.	3.35×10^{-5}	1.526
	Δ^3-Pentenoic acid.	2.09×10^{-5}	1.322
8	Δ^1-Cycloheptene carboxylic acid.	8.3×10^{-6}	0 919
	Δ^2-Cycloheptene carboxylic acid.	2.7×10^{-5}	1.432

6. Illustrations of True Rearrangements of Non-reversible Type.

The following table is a list of some of the more important true rearrangements of the non-reversible type. Many other illustrations of the rearrangements of Δ^2 unsaturated acids to their Δ^1 isomers are known for which no measurements of the ionization constants have been made. Yet in the light of the above discussion it is safe to conclude that they take place in the direction to decrease the free energy of ionization.

---

* See Section 5.

TABLE III.

True rearrangements (non-reversible type).

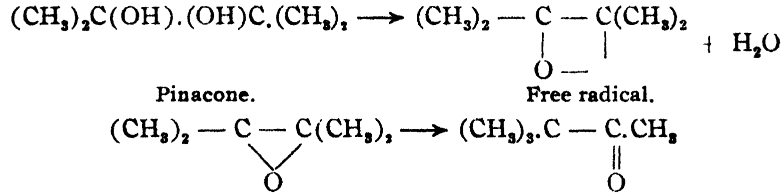
Class.	Before.	After.	Catalyzer.
1	Dihydrosorbic acid	Δ^1-Hexenoic acid	OH–
	Eugenol	Isoeugenol	OH–
2	Δ^2-Tetrahydrobenzoic acid	Δ^1-Tetrahydrobenzoic acid	OH–
	$\Delta^{3,5}$-Dihydrophthalic acid	$\Delta^{2,6}$-Dihydrophthalic acid	OH–
	* Δ^1-Tetrahydrophthalic acid	Δ^2-Tetrahydrophthalic acid	OH–
	Δ^2-Tetrahydroterephthalic acid	Δ^1-Tetrahydroterephthalic acid	OH–
	$\Delta^{2,5}$-Dihydroterephthalic acid	$\Delta^{1,5}$-Dihydroterephthalic acid	OH–
	$\Delta^{1,5}$-Dihydroterephthalic acid	$\Delta^{1,4}$-Dihydroterephthalic acid	OH–
	$\Delta^{2,6}$-Dihydroterephthalic acid	$\Delta^{1,4}$-Dihydroterephthalic acid	OH–
	$\Delta^{1,3}$-Dihydroterephthalic acid	$\Delta^{1,4}$-Dihydroterephthalic acid	OH–
	Aniline-*o*-sulphonic acid	Aniline-*p*-sulphonic acid	H_2SO_4 and heat
9	Acetohydroxycrotonic ester	Diacetoacetic ester	NaOOC.CH_3 and acetic anhydride
	Isoacetophenone ethyl ether	Phenylpropylketone	Boiling under pressure
13	Phenylmethylketoxine	Acetanilide	Acids
	(Beckmann's rearrangement)		Acid chlorides and anhydrides
14	Benzaldoxime-benzylether	Benzylbenzamide	Acid chlorides
	Methylaniline	*o*-Toluidine	Heat
	Alkyl iodides of aniline	Alkylated aniline hydroiodides	Heat
	Benzidine	Rearrangements*	H+
	Semidine	Rearrangements	H+

17	Alkyl isocyanides	Alkyl cyanides	Heat
18	Phenylpyrazole methyliodide	Phenylmethylpyrazole hydroiodide	Heat
	Alkyl pyridinium iodides	Alkyl pyridines	Heat
19	Diacetanilide	*p*-Acetoacetanilide	$ZnCl_2$
	p-Amino acetophenol	*p*-Hydroxyacetanilide	OH
	Diazamino compounds	Aminoazo compounds	Hydrochloride of amine
	Benzidine	Rearrangements	H+
	Semidine	Rearrangements	H+
	Methylaniline	*o*-Toluidine	Heat
	Nitrosamine of methylaniline	*p*-Nitrosomethylaniline	Heat
	Phenyl nitramine	*o*- and *p*-Nitraniline	Heat
	Phenyl sulphamic acid	Aniline-*o*-sulphonic acid	Acetic acid + H_2SO_4
	Diacyl anilide	*p*-Aceto-acetanilide	$ZnCl_2$
	Acyl haloanilides	*p*-Halo-acetanilides	Glacial CH_3COOH
	Phenyl hydroxylamine	*p*-Hydroxyaniline	Mineral acids
	Phenyl hydrazine	*p*-Phenylenediamine	Strong acids and heat
	Beckmann's rearrangements		Acids, acid chlorides, acid anhydrides
25	Benzoyl-*p*-hydroxyaniline	*p*-Hydroxybenzoylanilide	OH–
	Acetyl *p*-hydroxyaniline	*p*-Hydroxyacetanilide	OH–
	Aminophenylcarbonate	Phenolurethane	Heat
	Iminoether of formanilide	Ethyl formanilide	Heat
	Benzimido ethyl ether	Ethyl benzamide	Heat
	Cyanuric esters	Isocyanuric esters	Heat

* See Section 5.

7. Rearrangements with Reaction.

In Table IV a few examples of molecular rearrangements with reaction are given. The numbers in the first column of the table refer to the classes of Table V. With rearrangements of this type, it is much more difficult to distinguish any regular behavior. If such rearrangements are grouped according to the kind of reaction by which they are formed, some uniformity is obtained. Thus rearrangements taking place simultaneously with dehydration appear to be due to the fact that a free radical cannot exist for a measurable time or that a possible intermediate ring compound is too unstable toward rearrangement to exist. This is illustrated by the pinacone-pinacolin change:



$$(CH_3)_2C(OH).(OH)C.(CH_3)_2 \longrightarrow (CH_3)_2-\underset{|}{C}-\underset{|}{C}(CH_3)_2 + H_2O$$

Pinacone. Free radical.

$$(CH_3)_2-C-C(CH_3)_2 \longrightarrow (CH_3)_3.C-\underset{\|}{C}.CH_3$$

Unstable ring compound. Pinacolin.

In the case of the reduction of the unsaturated acids, the speed of the reaction and the strength of the reducing agent control the rearrangement. For example, if $\Delta^{1,3}$-dihydrobenzoic acid is reduced in the cold by sodium amalgam, the Δ^2-tetrahydro acid results, and there has been a shifting of the double union either from the Δ^1 or Δ^3 position to the Δ^2 position. If this same reaction is performed with the same reagents at a higher temperature the Δ^1-tetrahydrobenzoic acid results and there has been no shifting of either double union. A review of Fig. 1 and Tables I and II shows that the acid having two double unions within the molecule possesses more free energy of ionization than any of its dihydro reduction products. Further, the figure shows that the Δ^2 unsaturated acid has the greatest amount of free energy of ionization of any of its isomers. Hence, when Δ^2-tetrahydrobenzoic acid was formed by the reduction of $\Delta^{1,3}$-dihydrobenzoic acid, the decrease in the free energy of ionization was a minimum and a double union was shifted. With the same reagents, at a higher temperature, *i. e.*, where the speed of reaction was greater, reduction of the $\Delta^{1,3}$-dihydrobenzoic acid gave the Δ^1-tetrahydrobenzoic acid. The data for Fig. 1 show that the difference in the free energy of ionization of the $\Delta^{1,3}$ acid and its Δ^1-dihydro reduction product is much greater than in the case above where the Δ^2-dihydro reduction product was formed. Further, the formula for these acids show that there has been no shifting of the double union in the latter reduction. Therefore, *when the reduction of unsaturated acids containing more than one double union takes place so that the decrease in the free energy of ionization is a minimum, compounds form simultaneously*

TABLE IV

Class.	Rearrangements with reaction Before.	 After.	Reaction
1	Pinacone	Pinacolin	Dehydration
	3,3-Dimethyl butanol	Tetramethyl ethylene	Dehydration
	α,α-Dimethylglutaconic acid, 2	α,α'-Dimethylglutaric acid	Reduction
	Tetraphenylethylene	Benzoyl triphenyl methane	Oxidation
	Hydrobenzoin	Diphenylacetaldehyde	Dehydration
	Benzil	Benzilic acid	Hydration
	$\Delta^{1,3}$-Unsaturated acids (Open chain)	Δ^{2}-Unsaturated acids (Open chain)	Reduction
2	Triphenylmethane color bases	Triphenylmethane dyes	Dehydration
	Phenyl dimethyl indolinol	Dimethyl indole	Dehydration
	Gem-dimethyldihydroresorcinol	Dichloro-o-xylene	Chlorination
	$\Delta^{1,3}$-Dihydroterephthalic acid	Δ^{2}-Tetrahydroterephthalic acid	Reduction
	$\Delta^{1,4}$-Dihydroterephthalic acid	Δ^{2}-Tetrahydroterephthalic acid	Reduction of brominated acid
	$\Delta^{2,5}$-Dihydroterephthalic acid	Δ^{2}-Tetrahydroterephthalic acid	Reduction in cold
	Terephthalic acid	$\Delta^{2,5}$-Dihydroterephthalic acid	Reduction in cold
	α,α'-Dibromhexahydroterephthalic acid	$\Delta^{1,3}$-Dihydroterephthalic acid	Dehalogenation
	Phthalic acid	Δ^{2}-Tetrahydrophthalic acid*	Reduction + heat
	Benzoic acid	Δ^{2}-Tetrahydrobenzoic acid	Reduction
	$\Delta^{1,3}$-Dihydrobenzoic acid	Δ^{2}-Tetrahydrobenzoic acid	Reduction in cold
	$\Delta^{1,3}$-Dihydrobenzoic acid	Δ^{1}-Tetrahydrobenzoic acid	Reduction + heat
3	Triphenylmethane dyes	Tiyphenylmethane color bases	Hydration
	Isogeraniolene	v-Trimethylbenzene	Bromination and dehydration
	Isogeraniolene	Pseudocumene	Bromination and dehydration

* See Section 5

with a rearrangement and these compounds, in turn, will undergo rearrangement.

This class of rearrangements furnishes many fine illustrations of Ostwald's *law of successive reactions.*[1]

8. Review of the Field of Molecular Rearrangements.

The conclusions, given in the preceding paragraphs, are based on a general review of the field of molecular rearrangements. In this review, the need of a classification of the mass of material included under the term molecular rearrangement has been very evident. Not only should such reactions be classified as reversible and non-reversible rearrangements of the types discussed above, but the behavior of the different radicals should be thoroughly studied.

Classes of Known Rearrangements.

Table V has been developed to show the present state of the problem of rearrangement. In the first vertical column a partial list of the elements and radicals has been given. In the first horizontal row is given the elements between which the rearrangement occurs, while the second horizontal row gives their position in the compound, that is, whether in the ring or side chain. The third horizontal row gives the class to which each rearrangement of a given group is assigned. In the first horizontal row the letter stands for the atomic symbol of the element and the arrow shows the direction of the rearrangement. In the second row Op stands for open chain, R for closed chain or ring, Op ⟶ R for open or side chain to closed chain, and R ⟶ Op from closed to open or side chain. Thus to read the behavior of the alkyl group for class I, it is evident that the alkyl group will rearrange from carbon to carbon in the open chain; or for class 8, it is evident that the alkyl group may rearrange from carbon in the ring to oxygen in the side chain. Those rearrangements which are theoretically impossible because of the law of constant valence are designated by the sign x, while those impossible for the trivalent but possible for the pentavalent nitrogen are designated by the sign v.

To show the present state of knowledge of the phenomenon of rearrangements, the following system of marking is employed in the vertical columns beneath the classes:

o designates occasional occurrence,
c designates common occurrence, and
r designates rare occurrence.

Doubtless the above scheme is incomplete so far as the known cases are concerned, but it must be borne in mind that such a table when completed will demand many years of careful reading, especially in a field where systemization has not been attempted.

---

[1] Ostwald's *Lehrbuch*, II, 2, 445.

TABLE V.

Element or radical. Class.	C → C				C → O				O → C				C → N				N → C				O → O				O → N				N → O				N → N			
	Op	R	Op ↓ R	R ↓ Op	Op	R	Op ↓ R	R ↓ Op	Op	R	Op ↓ R	R ↓ Op	Op	R	Op ↓ R	R ↓ Op	Op	R	Op ↓ R	R ↓ Op	Op	R	Op ↓ R	R ↓ Op	Op	R	Op ↓ R	R ↓ Op	Op	R	Op ↓ R	R ↓ Op	Op	R	Op ↓ R	R ↓ Op
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Alkyl	o	o		o		x	x		o	x		x					c	c	c			x	x	x	c	x		x		x	x					
Aryl	c					x	x			x		x	c									x	x	x		x		x		x	x					
Acyl						x	x		o	x		x							c			x	x	x	o	x		x		x	x					
Aracyl						x	x		o	x		x										x	x	x	o	x		x		x	x					
Hydroxyl						x	x			x		x							c			x	x	x		x		x		x	x					
Oxyalkyl						x	x			x		x										x	x	x		x		x		x	x					
Oxyaryl						x	x			x		x										x	x	x		x		x		x	x					
Aldehyde						x	x			x		x										x	x	x		x		x		x	x					
Carbonyl						x	x			x		x										x	x	x		x		x		x	x					
Carboxyl						x	x			x		x										x	x	x		x		x		x	x					
Carboxyalkyl						x	x			x		x										x	x	x	r	x		x		x	x					
Carboxyaryl						x	x			x		x										x	x	x		x		x		x	x					
Amine						x	x			x		x							c			x	x	x		x		x		x	x					
Alkylamine						x	x			x		x										x	x	x		x		x		x	x					
Arylamine						x	x			x		x							c			x	x	x		x		x		x	x					
Nitro						x	x			x		x							o			x	x	x		x		x		x	x					
Nitroso						x	x			x		x							o			x	x	x		x		x		x	x					
Isonitroso					x	x	x	x	x	x	x	x		v	v			v		v	x	x	x	x	x	x	x	x	x	x	x	x		v	v	v
Hydrogen	c	c		c	c	x	x	c	c	x	o	x	c	c		c	c		c		c	x	x	x	c	x	x	x		x	x					
Halogen						x	x			x		x							c			x	x	x		x		x		x	x					
Sulphonic						x	x			x		x							c			x	x	x		x		x		x	x					
Double union	c	c	c	c	c	x	x	c	c	x	c	x	c	c		c	c		c			x	x	x	c	x		x	c	x	x					

TABLE VI.—ILLUSTRATION OF THE DIFFERENT CLASSES OF MOLECULAR REARRANGEMENTS GIVEN IN TABLE V.

Class.	Radical or element.	Rearrangement.	
		Before.	After.
1	Alkyl	Pinacone	Pinacolin
	Aryl	Tetraphenyl ethylene	Benzoyltriphenylmethane
	Hydrogen	Dihydrosorbic acid	Δ^1-Hexenoic acid
	Double union	Dihydrosorbic acid	Δ^1-Hexenoic acid
2	Alkyl	*gem*-Dimethyldihydroresorcinol	Dichloro-*o*-xylene
	Hydrogen	Δ^2-Tetrahydrobenzoic acid	Δ^1-Tetrahydrobenzoic acid
	Double union	Δ^2-Tetrahydrobenzoic acid	Δ^1-Tetrahydrobenzoic acid
	Sulphonic	Aniline-*o*-sulphonic acid	Aniline-*p*-sulphonic acid
3	Double union	Fuchsine	Rosaniline
4	Double union	Rosaniline	Fuchsine
5	Hydrogen	Enol-acetoacetic ester	Keto-acetoacetic ester
8	Hydrogen	Keto-phloroglucinol	Enol-phloroglucinol
	Double union	Enol-phloroglucinol	Keto-phloroglucinol
9	Alkyl	Isoacetophenone ethyl ether	Phenylpropylketone
	Acetyl	Acetohydroxycrotonic ester	Diacetoacetic ester
	Benzoyl	Acetophenone-*o*-benzoate	Dibenzoylmethane
	Hydrogen	Keto-acetoacetic ester	Enol-acetoacetic ester
	Double union	Keto-acetoacetic ester	Enol-acetoacetic ester
11	Hydrogen	Enol-phloroglucinol	Keto-phloroglucinol
	Double union	Keto-phloroglucinol	Enol-phloroglucinol
13	Aryl	Phenylmethyl ketoxime	Acetanilide
	Hydrogen	Tautomerism—Amide	Imide type
	Double union	Tautomerism—Amide	Imidol type
14	Hydrogen	Phenylpyrazolone methyl iodide	Phenylmethylpyrazole
16	Hydrogen	Methylaniline	*o*-Toluidine
	Double union	Rosaniline	Fuchsine
17	Alkyl	Alkyl isocyanides	Alkyl cyanides
	Aryl	Phenyl isocyanide	Benzonitrile
	Hydrogen	Tautomerism—Imide	Cyanide type
18	Alkyl	Phenylpyrazole methyl iodide	Phenyl methyl pyrazole
19	Alkyl	Methylaniline	*o*- and *p*-Toluidines
	Acyl	Diacetanilide	*p*-Acetylacetanilide
	Hydroxyl	Phenylhydroxylamine	*p*-Aminophenol
	Amine	Phenyl hydrazine	*p*-Phenylenediamine
	Arylamine	Hydrazobenzene	Benzidine
	Nitro	Phenyl-nitramine	*o*- and *p*-Nitraniline
	Nitroso	Nitrosamine of methylaniline	*p*-Nitrosomethylaniline
	Hydrogen	Tautomerism—Azo	Hydrazo type
	Halogen	Acylchloranilides	*p*-Chloroacetanilides
	Sulphonic	Sulphamic acid	Aniline-*o*-sulphonic acid
	Double union	Fuchsine	Rosaniline
21	Hydrogen	*p*-Nitrophenol	*p*-Isonitrophenol
25	Alkyl	Imino ether of formanilide	Ethyl formanilide
	Acyl	*p*-Aminoacetophenol	*p*-Hydroxyacetanilide
	Benzoyl	*p*-Amino-benzoylphenol	*p*-Hydroxybenzanilide
	Carboxyalkyl	Amino-phenylcarbonate	Phenol urethane
	Hydrogen	Tautomerism—Amide	Imidol type
29	Hydrogen	Tautomerism—Amide	Imidol type

This table, in conjunction with Tables III and IV, shows that hydrogen, the double union (which in general is the same thing as the shifting of hydrogen) and the alkyl group are more generally rearranged than the other elements or radicals. Further, rearrangements occur much more frequently between nitrogen and carbon, the shifting occurring from sidechain nitrogen to ring carbon. The alkyl, acyl, aromatic acid radical, hydroxyl, amine, alkylamine, arylamine, nitroso, nitro, halogen and sulphonic radicals undergo this rearrangement (members of class 19). In general, however, the oxyalkyl, oxyaryl, and alkyl, aryl, nitro, nitroso, and haloamine groups do not rearrange as a whole, but rather the alkyl, aryl, nitro, nitroso and halogens shift from the oxygen or nitrogen to carbon.

The classes given in the tables, refer to this scheme of classification, and Table VI gives illustrations of rearrangements of different elements and radicals belonging to these classes.

Summary.

1. Molecular rearrangements of carbon compounds are of the reversible and non-reversible types of chemical reactions.

2. Molecular rearrangements of carbon compounds must be further classified according as the rearrangement is simply a readjustment of the atoms already present in the molecule (true rearrangements) or as the rearrangement is due to atoms having been added to or taken away from the original molecules (rearrangements with reaction).

3. Compounds which rearrange are formed under conditions where the speed of formation is a minimum so as to produce substances very unstable toward arrangements.

4. The reagents present when a compound undergoes true rearrangement of the non-reversible type are catalytic to the speed of the rearrangement.

5. True rearrangements of the non-reversible type take place in the direction to produce substances more stable toward rearrangement.

6. True rearrangements of acids and bases belonging to the non-reversible type take place in the direction to produce acids and bases more stable toward ionization (*i. e.*, having less free energy of ionization) and therefore the logarithm of the ionization constant may be used as a criterion of stability in these rearrangements.

7. An organic acid, which possesses a double union Δ^2 to its carboxyl group, has a greater free energy of ionization than any of its isomers and may, therefore, readily undergo rearrangements to produce isomers more stable toward ionization and rearrangement.

8. Δ^2 Unsaturated acids are formed from $\Delta^{1,3}$ unsaturated acids under the conditions where the speed of formation is a minimum, the de-

crease in the free energy of ionization is a minimum, and the stability toward rearrangement is a minimum.

9. Many rearrangements with reaction are due to the fact that a free radical cannot exist, and after certain atoms or groups have been eliminated the very unstable radical resulting undergoes a readjustment of the atoms present so as to maintain the quadrivalent nature of carbon and produce a substance more stable toward rearrangement.

10. A schematic review of the field of molecular rearrangements of carbon compounds is given by Table V, and Table VI gives illustrations of the classes of rearrangements designated in Table V.

The author wishes to thank Dr. W. A. Noyes, of the University of Illinois, for his kind suggestions and criticisms of this paper and also Dr. W. C. Bray, of Massachusetts Institute of Technology, for his kind suggestions regarding Section 4.

[Contribution from the Bureau of Chemistry, U. S. Dept. of Agriculture.]

THE INVERSION OF CANE SUGAR BY INVERTASE. VII. THE EFFECT OF ALCOHOL ON INVERTASE.

By C. S. Hudson and H. S. Paine.

Received July 11, 1910.

Purpose of the Investigation.

A knowledge of the action of alcohol on invertase is of practical importance for two reasons: first, alcohol is naturally present during the fermentation of cane sugar by yeast and the invertase of the yeast is thus normally in the presence of weak alcohol; and, second, alcohol is often used, though generally with little success, to prepare the enzyme in a solid form by precipitation from an aqueous extract of yeast. In order to learn what influence alcohol of different strengths has on invertase, the following investigation was made. The results show that the influence is exceedingly great and that it consists in three distinct actions, namely, an inactivation, a permanent destruction, and a precipitation of the enzyme. These actions will be described in the order named.

The Inactivation of Invertase by Alcohol.—The activity of purified invertase in inverting cane sugar dissolved in various strengths of ethyl alcohol was measured at 30° by the usual method. Care was taken to have sufficient acetic acid in the solutions to insure that the maximum activity of the enzyme was attained, and the solutions were made alkaline at the end of the experiment to stop the enzymatic action and complete the mutarotation. The alcohol used was Squibb's or Baker's absolute alcohol and the concentrations are expressed as volume per cent. The activities are recorded in Table I as the velocity coefficients of the inversion, using minutes and decimal lagarithms and multiplying by

10,000 to avoid decimals. The results are also expressed graphically in Fig. 1.

It is apparent that alcohol has a strong inactivating action on invertase even when the alcohol is dilute. The destruction of invertase by alcohol does not take place below about 20 per cent., as will be shown under the following caption, but the activity of the enzyme is markedly lowered by even a few per cent. of alcohol. The figure shows that the relation between alcoholic strength and activity is not proportionality but may be represented as a logarithmic or hyperbolic function. On account of the fact that rapid destruction of the enzyme takes place in solutions above 30 per cent. alcoholic strength it is not possible to measure the activity of invertase in this region by the usual method; the theory of the modified procedure which has accordingly been used to measure the activity in 50 and 70 per cent. alcohol is given on page 1355 and the values which were found are included in the table and figure.

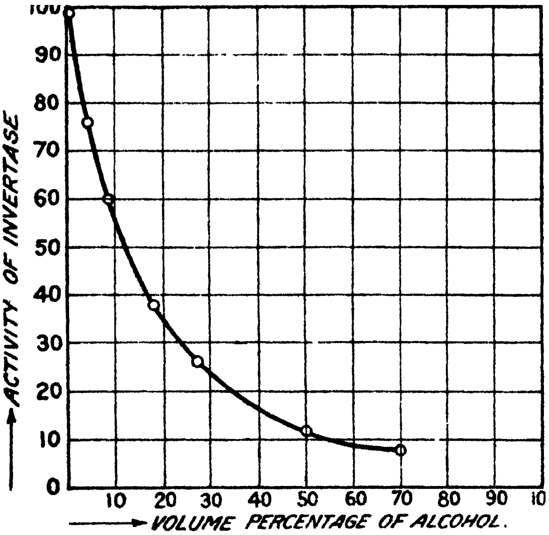


Fig. 1.—The influence of alcohol on the activity of invertase.

The inactivation of invertase by alcohol was noticed by O'Sullivan and Thompson,[1] and they state that the inactivation by alcohol is "in direct proportion with the amount present. Five per cent. alcohol decreases the speed of the reaction by about one-half." The results here given are somewhat different in detail from those quoted, because we have measured the inactivation for higher strengths of alcohol than were used by the previous investigators. It will be noticed that our results also show almost a linear relation between activity and alcohol strength for weak alcoholic solutions.

---

[1] *J. Chem. Soc.*, 27, 927 (1890).

TABLE I.—ACTIVITY OF PURIFIED INVERTASE IN AQUEOUS ALCOHOL.

(Temperature 30°. Concentrations: Aqueous alcohol containing cane sugar 0.2 normal, and acetic acid 0.02 normal; 100 cc. of this mixture were added to 10 cc. of purified invertase solution.)

Concentration of alcohol (volume per cent.).	Activity invertase K_1 (10,000).	Percentage activity.
0.0	80.0	100
4.3	61.0	76
9.1	48.0	60
18.2	30.0	38
27.3	21.0	26
50.0	8.8	11
70.0	6.4	8

The Destruction of Invertase by Alcohol.—The measurements of the destruction of invertase by alcohol were made by the method previously used in studying the destruction of the enzyme by acids and alkalies.[1] The rate of the destruction follows the course of unimolecular reactions, as is shown by the following experiment. The value of the velocity coefficient of the unimolecular formula, k_2, remains constant within the errors of experiment during the course of the destruction.

TABLE II.—UNIMOLECULAR ORDER OF THE DESTRUCTION OF INVERTASE BY ALCOHOL.

(Temperature 30°. Alcohol 20 per cent. by volume. Maximum activities were measured.)

Time. Minutes.	Activity of invertase [k_2 (10,000)].	Velocity coefficient (k_2).
0	8.98	.....
15	8.11	0.00295
30	7.33	0.00294
45	6.54	0.00306
75	5.41	0.00293
105	4.66	0.00271
165	4.13	0.00204
	Average,	0 00277

The rates of destruction of invertase which were found in various strengths of alcohol are recorded in Table III, the values of k_2 being expressed in minutes and decimal logarithms and multiplied by 1,000 to avoid decimals. The results are also shown graphically in Fig. 2.

The rate of destruction changes most peculiarly with the strengths of the alcohol, reaching a pronounced maximum at about 50 per cent. Presumably the protective action of strong alcohol is due to its precipitating the invertase, or some other substance whose precipitation protects the

---

[1] THIS JOURNAL, 32, 778 (1910),

TABLE III.—RATES OF DESTRUCTION OF INVERTASE BY ALCOHOL.

Concentration of alcohol (volume per cent.).	Rate of destruction [$k_2 \times (1{,}000)$].	Concentration of alcohol (volume per cent.).	Rate of destruction [$k_2 \times (1{,}000)$]
0	0	50	850
10	0	55	570
20	3	60	240
30	44	70	74
40	260	80	7
45	487	90	2

invertase, as a visible precipitation begins at or near the strength of 50 per cent., at which the maximum of the curve falls and the protective action begins. If the curve to the left of the maximum is alone regarded as the curve of the destruction in solution, it is noticed that it is very similar to the curve for the destruction of the enzyme by acids and alkalies.[1] It appears, therefore, that the destruction by alcohol in homogeneous solution is due to a decomposition of the invertase similar to the hydrolytic decompositions that are presumably the cause of the destruction by acids and alkalies. The practical application of the results on alcoholic precipitation is given on page 1356.

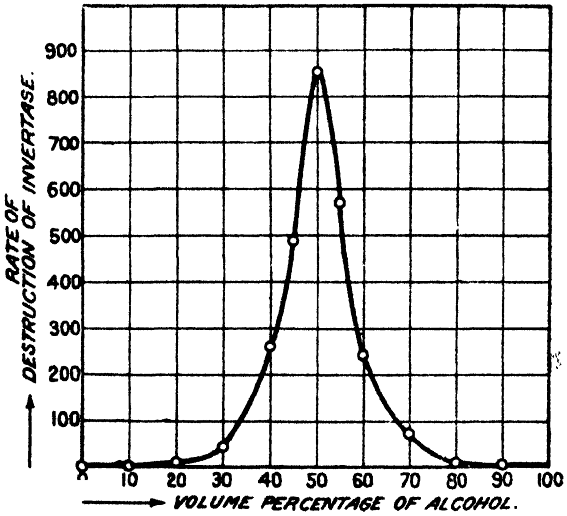


Fig. 2.—The destruction of invertase by alcohol.

The Action of Cane Sugar in Preventing the Destruction of Invertase.—In order to learn whether cane sugar protects invertase from destruction by alcohol, the rate of destruction in a 0.2 normal solution of cane sugar in 50 per cent. alcohol was measured at 30° by the method already described. A correction was applied for the rotation of the sugar in the samples as they were removed to test their activities. The method of preparing the mixture of cane sugar, aqueous alcohol, invertase, and acetic acid is shown in the description of the experiment recorded in Table V; the results on the rate of destruction are given in Table IV:

---

[1] THIS JOURNAL, 32, 779.

TABLE IV.—RATE OF DESTRUCTION OF INVERTASE IN 50 PER CENT. ALCOHOL CONTAINING 6 PER CENT. OF CANE SUGAR.

Time Minutes.	Activity of sample (k_1).	Velocity coefficient (k_3)
0	0.00049	...
30	0.00024	0.010
60	0.00016	0.008
	Average,	0.009

The rate of destruction is far less than that shown for 50 per cent. alcohol in Table III, namely 0.850. The cause of this difference can lie only in the fact that cane sugar was not present in the latter experiments. Several other experiments have given results agreeing with these in showing that cane sugar exerts a very strong influence in protecting invertase from destruction by alcohol. O'Sullivan and Tompson[1] have shown that cane sugar protects invertase from destruction by hot water, and it is well known among distillers that diastase is not so easily destroyed by hot water, if maltose is in the solution; it is then an analogous fact that cane sugar protects invertase from the action of alcohol. The most plausible explanation is that these sugars combine with the enzyme, and the resulting compound is not so easily attacked by alcohol or hot water.

Theory of t[illegible] Rate of Inversion of Cane Sugar during the Destruction of the Invertase.

The rate of inversion of cane sugar by invertase in dilute solution follows the unimolecular order, and it has just been shown that the rate of destruction by alcohol does the same. If invertase is added to a solution of cane sugar in aqueous alcohol of a strength which destroys the enzyme, there occur two simultaneous reactions, the inversion of the cane sugar and the destruction of the invertase. The theory of these dependent or coupled reactions is as follows: At constant temperature start with a solution containing A gram molecules of cane sugar per liter and I units of invertase. After the lapse of t minutes let there be in the solution i units of invertase and $(A - x)$ gram molecules of cane sugar. The rate of destruction of the invertase is

$$-di/dt = k_2 i, \tag{1}$$

in which k_2 is the velocity coefficient of the destructive reaction. The integral of Equation 1 under the condition that $i = I$ when $t = O$ is

$$i = Ie^{-k_2 t}. \tag{2}$$

---

[1] *J. Chem. Soc.*, 57, 900 (1890).

The rate of inversion of the cane sugar is

$$dx/dt = k_1\,(A - x)\,i/I = k_1\,(A - x)\,e^{-k_2t}, \tag{3}$$

where k_1 is the velocity coefficient of the inversion when I units of invertase are present. The integral of Equation 3 under the condition that $x = O$ when $t = O$ is

$$\log A/A - x = k_1/k_2\,(1 - e^{-k_2t}). \tag{4}$$

Equation 4 has been used in finding the velocity of inversion of cane sugar by invertase (k_1) in 50 per cent. alcohol. A mixture of 600 cc. of 0.2 normal cane sugar solution in 55 per cent. alcohol (which was also 0.02 normal with respect to acetic acid) with 60 cc. of dialyzed invertase solution was kept at 30° and the progress of the inversion measured polarimetrically from time to time, the samples being made alkaline before each reading of the rotation. In Table V the rate of this incomplete inversion of cane sugar by invertase in 50 per cent. alcohol is recorded. The quantity of cane sugar present (A) is expressed in degrees, $A = 48.1\,(1.267)^1 = 61.6$, and the quantity of cane sugar present at any time t is $A - x = r + 48.7\,(0.267)$, where r is the reading of the solution. The value of k_2 is taken from Table IV as 0.009.

TABLE V.—COURSE OF THE INCOMPLETE INVERSION OF CANE SUGAR BY INVERTASE IN 50 PER CENT. ALCOHOL

Time Minutes	Rotation (°)	$k_1 = \frac{k_2}{1 - 10^{-k_2t}} \log \frac{A}{A - x}$
0	48.7	
15	44.8	0.00094
30	42.3	0.00091
45	40.9	0.00087
60	39.9	0.000[illegible]
90	38.5	0.00083
120	37.7	0.00083
240	36.0	0.00086
360	35.6	0.00094
	Average,	0.00088

The values of k_1 in the last column, as calculated from Equation IV, are sufficiently constant to show that the reaction follows the laws that were assumed in the theory, within the limits of the present experimentation. It was found that the activity of the invertase when no alcohol was present was $k_1 = 0.0080$. If this rate in pure water is taken as 100, the rate in 50 per cent. alcohol is then 11. Similar experiments have shown that in 70 per cent. alcohol the rate of inversion, on the basis of 100, is 8. These values for the activity in 50 and 70 per cent. alcohol are included in Table I.

The Precipitation of Invertase by Alcohol.—Alcohol precipitates inver-

---

[1] The Clerget factor at 30°; see *J. Ind. Eng. Chem.*, 2, 144 (1910).

tase,* and it is in this way possible to prepare a solid enzyme, though nothing regarding its purity can be predicated at present. It is a fact, however, that such solid invertase preparations are usually of low enzymatic activity. The reason for this is apparent from the results of this investigation, for unless the alcoholic precipitation is performed in very strong alcoholic solution, the invertase is rapidly destroyed by the alcohol. There are three ways by which this destruction can be lessened: one is to use strong alcohol in large proportion, another is to work at low temperatures, and the third is to have cane sugar present in the solution to protect the invertase from destruction. In order to test the first method, 50 cc. of invertase liquor which had been dialyzed until it contained only 1 per cent. of total solids was mixed with 500 cc. of 95 per cent. alcohol at 25°, and after half an hour the coagulated precipitate was filtered off, washed with alcohol, then with ether, and dried over sulphuric acid in a desiccator. The mass, which resembled horn in superficial appearance, was dissolved in 50 cc. of water, and its inverting activity was found to be 78 per cent. of that of the original sample. The second method of precipitation, at low temperature (0°), gave a small recovery and is not to be recommended.

In order to test the protective action of cane sugar, 25 grams of it were dissolved in 50 cc. of dialyzed invertase and 95 per cent. alcohol added until the strength of the mixture became 70 per cent. alcohol. The precipitate was filtered off, washed with ether, and dried in a desiccator. On redissolving, it showed 94 per cent. of the original activity and a second experiment gave a recovery of 96 per cent. These experiments demonstrate that it is possible to precipitate invertase with alcohol without any important loss of activity provided the enzyme is protected by cane sugar. Other sugars may have this protective action also, but this point has not yet been investigated.

Summary.

O'Sullivan and Tompson's observation that alcohol reduces the activity of invertase is confirmed, and the relation between alcoholic strength and inactivation is shown to be graphically a rounded curve (Fig. 1). Alcohol is found to destroy invertase, and the relation between alcoholic strength and rate of destruction is very peculiar, as it shows a high maximum at about 50 per cent. alcohol. The destruction follows the course of unimolecular reactions; it is not noticeable below 20 per cent. alcohol at 30°, is almost instantaneous at 50 per cent., and decreases to nearly zero at 80 per cent. (Fig. 2). If the alcohol contains cane sugar, the destruction is much slower; thus, 6 per cent. cane sugar reduces the rate of destruction in 50 per cent. alcohol from 0.850 to 0.009, or to about 1 per cent. of its original value. A mathematical theory of the progress of the inversion of cane sugar by invertase in alcoholic solution of sufficient

strength to slowly destroy the enzyme has been worked out and its conclusions are found to agree with the results of the experiments. In this way it has been possible to measure the activity of invertase in 50 and 70 per cent. alcohol, where the destruction plays an important role. Invertase can be precipitated by alcohol without much destruction, provided the strength of alcohol in the final solution is high, approximately 90 per cent. By this method of precipitation, working at room temperature, a solid preparation was obtained which had 78 per cent. of the activity of the original solution. . If cane sugar is present, invertase can be precipitated with no important destruction by even 70 per cent. alcohol; this method of precipitation gave a recovery of 94 and 96 per cent. of the original activity.

[FROM THE STORRS AGRICULTURAL EXPERIMENT STATION.]

THE CATALASE OF MOLDS.

BY ARTHUR W. DOX.

Received June 22, 1910.

An enzyme which accelerates the decomposition of hydrogen peroxide with the liberation of oxygen in a molecular form seems to be almost universally present in living tissues. Its presence in animal organs, in blood, and in milk has been widely investigated. In the vegetable kingdom its occurrence in green plants and in certain fungi is well known.

Many of the basidiomycetes, as well as the yeasts and bacteria, have been found by numerous investigators to contain catalase. The molds, however, have received but little attention with reference to their catalase content. Bach and Chodat[1] found catalase in *Sterigmatocystis nigra*, and Pringsheim[2] noted its presence in the press juice of fifteen out of the seventeen species of mold examined by him. No other investigators seem to have given any attention to the catalase of this important group of fungi.

Catalase is quite distinct from the oxidizing enzymes known as oxidase and peroxidase, though both of these are probably dependent for their oxidizing power upon the presence of some peroxide, either in the plant itself or added in the form of hydrogen peroxide. In the case of the oxidizing enzymes, the oxygen seems to be liberated in a nascent or active form, which readily acts upon oxidizable substances, such as leuco bases, guaiaconic acid, phenolphthalin, etc., and the reaction at once made apparent by the color of the product of oxidation.

Although the molds investigated by the writer showed only slight evidence of oxidase or peroxidase, catalase was generally present in greater concentration. Many of these fungi produce colored spores or secrete a colored substance into the medium, making the color reactions for oxidizing enzymes rather difficult of demonstration. With guaiaconic acid little or no production of color was noticed, though hydroquinone seemed to be acted upon somewhat more readily. Catalase was first observed in the desiccated mycelium which furnished the basis of the studies of other enzymes by the writer.[1]

---

[1] *Ber.*, 36, 1756 (1893).

[2] *Z. physiol. Chem.*, 62, 386 (1909).

Experimental.

Most of these experiments were conducted with *Penicillium camemberti*, the well-known mold which ripens Camembert cheese. The organism was grown in pure culture upon a synthetic fluid containing *d*-glucose and inorganic salts. One hundred cc. of the medium were placed in each of a series of 300 cc. Erlenmeyer flasks. The flasks were closed with a cotton plug, then sterilized in an autoclave and inoculated with spores of *P. camemberti*. Determinations were made on successive days, a fresh culture being used each time. To distinguish between intra- and extracellular enzymes, both the mycelium and the filtered medium were tested. The mycelium was ground to a fine paste, suspended in 100 cc. water and 10 cc. taken for the determination. The same proportion of the medium (10 cc.) was taken for the extracellular determinations.

The form of apparatus used for measuring the gas liberated was an ordinary Schiff nitrometer. This was connected by means of a rubber tube with a small glass cylinder containing the enzyme solution and a small dish of hydrogen peroxide (5 cc.) floating on the solution. By shaking the cylinder the enzyme and peroxide are brought in contact, and the gas liberated displaces the water in the nitrometer. This method of measuring directly the volume of gas liberated in a given time was found more satisfactory in this case than Sentner's method of titrating the excess of peroxide with potassium permanganate. Owing to the presence of sugar and perhaps other reducing substances in the medium, the blank that had to be deducted when Sentner's method was used was so high as to introduce considerable error.

The peroxide used was the commercial preparation known as "Dioxygen." One cubic centimeter reduced 22.4 cc. of decinormal permanganate solution, showing that the strength was 3.81 per cent. by weight or 12.5 volume per cent.

In addition to the enzyme determinations, the nitrogen in an aliquot portion of the mycelium was determined, also the optical rotation of the medium, in order to compare the enzymatic activity with the stage of development of the fungus and the supply of nutriment remaining in the medium. The results for *P. camemberti* are tabulated below. The gas volumes are expressed at 0° and 760 mm. pressure.

---

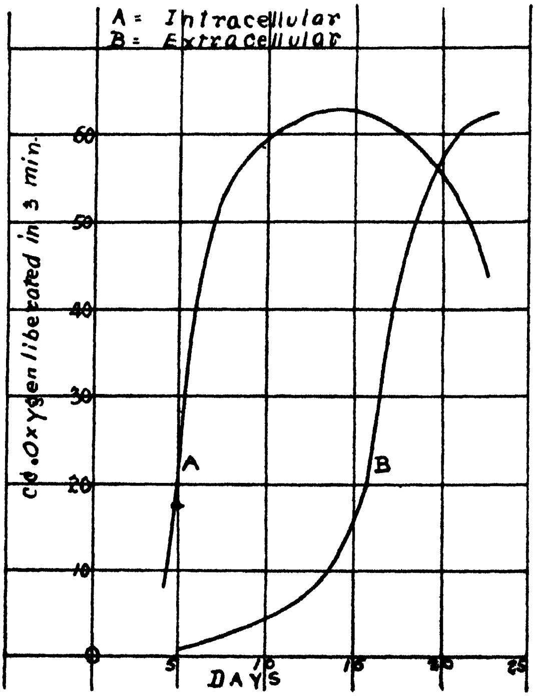
[1] *Bulletin No.* 120, *Bureau of Animal Industry*, Washington, 1910.

	Catalase			
Age of culture. Days.	Intracellular C_2 in 3 min. cc	Extracellular O_2 in 3 min. cc	Nitrogen in mycelium. Gram	Rotation. of medium. Ventzke.
0	0 0	0 0	0 000	9·5
4	8 1	0 0	0 009	8.8
5	17 1	0 5	0 012	8.2
6	30 7	1.2	0 018	7 4
7	52 0	1.9	0 025	5·5
8	54 0	2 9	0 030	4·3
9	58 0	3 7	0 030	3 1
10	60 1	4·1	0.031	2 7
11	61 5	5 1	0 031	2.2
12	62 0	6.5	0 031	1 8
13	63 3	7·5	0 031	1 5
14	63 1	12 7	0 031	0 07
15	61 7	13 1	0 030	0 7
16	61 4	21 5	0 030	0 3
17	60 7	37 4	0 029	0 1
18	60.7	47 8	0 028	0 0
19	59 4	50 5	0 027	
20	56 1	57 2	0 027	
21	52 8	60 9	0 027	
22	50 8	61 1	0 026	
23	43 0	60 7	0 026	
24	42 5	61 1	0 025	
25	41 2	60 9	0.023	

As soon as the mold made its appearance on the surface of the culture medium, the mycelium was found to contain a very active catalase. The increase on succeeding days does not represent a percentage increase, but is due rather to the greater amount of mold as shown by the appearance of the culture as well as by the nitrogen determinations. After about fifteen days, when the culture is mature, the intracellular enzyme gradually decreases. This change is accompanied by a loss of nitrogen from the mycelium and a gradual decrease of turbidity of the fungus cells. In fact, after the culture is a month old the mycelium can be disintegrated by simply shaking the flask. The decrease in intracellular catalase is not to be regarded, therefore, as an actual loss in activity of the enzyme, but rather as the change from the intra- to the extracellular form.

The enzyme in the medium or extracellular enzyme increased steadily during the entire time that the cultures were under observation. This increase continued after the enzyme in the mycelium had begun to decrease and the carbohydrate was completely exhausted from the medium. The medium was always perfectly clear after filtering off the mold. Its activity was not appreciably impaired when it was freed from the mycelium and preserved two weeks with toluene. But on heating the liquid to boiling its activity was completely destroyed.

The relation between intra- and extracellular catalase can best be shown graphically. As the amount of oxygen approaches the theoretical yield, however, the differences in enzyme activity from day to day, as shown by the figures recorded, are much less striking than is actually the case. Unless this is borne in mind the following curve, where the amount of oxygen liberated is plotted against the time during which the culture has grown, is apt to be somewhat misleading. The curve in the main shows the relation between age of culture and enzyme activity, except that the summit is unduly flattened.



Both the intra- and extracellular catalase are somewhat diffusible through parchment and collodion membranes. In performing the test with the endo enzyme, the cellular débris was not completely removed, and there is a possibility that during the course of the experiments, some of this enzyme may have changed to the extracellular form and passed through the membrane as such. Conclusive experiments as to the diffusibility of the intracellular enzyme can best be made with the so-called press-juice, the means of preparing which were not at the writer's command.

In order to determine how widely catalase is distributed in this group of fungi, cultures of a number of species were made, and the catalase in the medium determined at the end of two months. The molds were grown in test tubes on 10 cc. of the fluid medium. The liquid was filtered, and 5 cc. diluted with 10 cc. water were tested with 2 cc. of peroxide.

Species.	Cc. oxygen in 3 min.
Penicillium duclauxi	25.3
biforme	25.0
spinulosum	22.4
decumbens	17.4
camemberti	13.7
italicum	11.1
chrysogenum	10.0
stoloniferum	8.6
intricatum	5.2
atramentosum	3.5
lilacinum	2.8
citrinum	2.6
expansum	2.0
divaricatum	1.2
rugulosum	0.9
roseum	0.8
africanum	0.8
claviforme	0.3
pinophilum	0.2
luteum	0.2
roqueforti	0.2
granulatum	0.0

Species.	Cc. oxygen in 3 min.
Aspergillus glaucus	21.1
fumigatus	19.6
clavatus	13.2
nidulans	10.1
varians	7.4
flavus	6.5
ostianus	4.5
ochraceus	3.9
oryzae	2.4
candidus	1.2
wentii	0.6
niger	0.0

In this experiment the formation of extracellular catalase took place much less rapidly on account of the greater depth of the culture medium as compared with the mold-covered surface. In no case was the sugar completely used up, for the filtrate invariably gave a heavy precipitate of cuprous oxide on boiling with Fehling's solution. The above table shows, however, that nearly all of the species examined secrete a catalase into the medium. Nevertheless there are striking differences in the amount produced by the various species. These variations can hardly be attributed to differences in the vigor of the cultures, for all of the species grew well upon this medium and formed a dense mycelium with normal fruiting bodies.

From the experiments described in this paper it is evident that molds contain the enzyme catalase, first in the intracellular form, then gradually allow it to escape into the medium as an extracellular enzyme. Just how this change is effected is not definitely known as yet, but it seems probable that some of the fungus cells undergo disintegration, or at least a loss of vitality, by which an opportunity is afforded the enzymes for diffusion or mechanical release into the medium.

NOTE.

The Instability of Alloxan.—The notes by Professor Wheeler and Professor Bogert on the instability of alloxan in the June number of the JOURNAL recall an experience of my own with the same substance. On attempting some years ago to open a small glass-stoppered bottle containing alloxan I found the stopper so firmly fixed that it was impossible to remove it by any of the methods usually employed in such cases. I then proceeded to scratch a mark on the neck by means of a file, when the bottle exploded with a loud report, but with no damage other than scattering glass and the contents of the bottle over a considerable area of the working table and floor of the laboratory. My conclusion at the time was that the explosion was caused by an accumulation of gases resulting from the slow decomposition of the alloxan in a bottle with a tightly fitting stopper. EDWARD C. FRANKLIN.

LELAND STANFORD, JR., UNIVERSITY.

NEW BOOK.

Notions fondamentales de chimie organique. By CH. MOUREU, professeur à l'École supérieure de Pharmacie de l'Université de Paris, troisième édition, revue et mise au courant des derniers travaux. Paris. Gauthier-Villars. 1910. 354 pp.

The new edition of this excellent introduction to the study of organic chemistry follows along the same general lines as its predecessors.[1] The subject matter of the second edition has been revised and considerable new material added, to bring the book as nearly as possible up to date. This is evident in the space accorded to catalytic processes and to the developments of the Grignard reaction, and in the inclusion of the results of recent investigations on osmotic pressure and molecular refraction, as well as such newer classes of compounds as the ketenes, ozonides, and the like. A full index constitutes a very welcome addition. The book can be cordially commended. MARSTON TAYLOR BOGERT.

RECENT PUBLICATIONS.

ABDERHALDEN, E.: **Fortschritte der naturwissenschaftlichen Forschung.** Berlin: Urban & Schwarzenberg, I. Bd., 10 M.

ALBE, E. E.: **The Electron Theory.** Third edition. New York: Longmans, Green & Co., 327 pp., $1.25.

ANDERSEN, F.: **Hilfsbuch für Wärme und Kälteschutz.** Berlin: Jul. Springer, 3.60 M.

ANSELMINO, O.: **Das Wasser. Experimentalvorträge.** (Chemie des Wassers; Reinigung des Wassers; Trinkwasser; etc.). Leipzig: 8°, 128 pp., 1 M.

v. ARLT, F. R.: **Laboratoriumsbuch für die Zementindustrie.** W. Knapp: Halle a/S, 4.50 M.

---

[1] See THIS JOURNAL, 29, 99 (1907).

Arrhenius, S.: **Die Atmosphäre der Planeten.** Leipzig: Akademische Verlagsgesellschaft, 1.20 M.

Barus, C.: **Condensation of Vapor as Induced by Nuclei and Ions.** Washington: 84 pp., 75 cents.

Bauer, A.: **Zur Geschichte des Tellurs.** Wien. 8°, 12 pp., 1 M.

Bauriedel, F.: **Untersuchung über das Platin Hexabromoplatineate organischer Ammoniumbasen.** Nürnberg: M. Edelmann, 36 pp., 1.50 M.

Benthaus, W.: **Ueber braunes amorphes Silicium.** Hildesheim: August Lax, 75 pp., 2 M.

Berlin, P. **Die Bayerische Spiegelglasindustrie.** Berlin: Emil Ebering, 8°, 144 pp., 3.50 M.

Bersch, W.: **Hefen, Schimmelpilze und Bakterien.** Wien: A. Hartleben, 6.80 M.

Betts, A. G.: **Bleiraffination durch Elektrolyse.** Halle, 8°, 298 pp., 18 M.

Brochet, A.: **La soude électrolytique.** Paris: B. Tignol, 8°, 10 Fr.

Brown, J.: **Der elektrische Ofen im Dienste der keramischen Industrie.** Halle, 8°, 373 pp, 22 M.

Buchner, G.: **Die Metallfärbung.** 4 Aufl. Berlin: M. Krayn, 8.70 M.

Christiansen, C, and Müller, J J.: **Elemente der Theoretischen Physik.** 3 verb Aufl. Leipzig: J A. Barth, 8°, 690 pp., 15 M.

Collis, E L: **Lead Smelting.** London: Wyman & Sons.

Crinon, C.: **Revue des médicaments nouveaux et de quelques médications nouvelles.** Paris: Vigot Freres, 4. Fr.

Dennert, E.: **Das chemische Praktikum.** Hamburg: Leopold Voss, 4 verb. Aufl., 1.20 M.

Duclaux, J.: **La chimie de matière vivante.** Paris: F. Alcan, 16, 3.50 Fr.

Dyer, B. **Fertilizers and Feeding Stuffs.** Sixth edition. London: Crosby, Lockwood & Son.

Einheitsmethoden zur Untersuchung von Fetten, Oelen, Seifen und Glycerinen sowie sonstigen Materialien der Seifenindustrie. Berlin: J. Springer, 2.40 M.

Erdmann, H: **Lehrbuch der anorganischen Chemie.** 5 Aufl. Braunschweig: Vieweg & Sohn, 11.60 M.

Ewing, J. A.: **Die mechanische Kälteerzeugung.** Braunschweig: F. Vieweg & Sohn, 8.50 M.

Fess, F., and Steyer, G.: **A. Reconnaissance of the Gypsum Deposits of California.** W. Wesley, 36 pp., 3 s.

Fischer, B.: **Kurzgefasste Anleitung zu den wichtigeren hygienischen Untersuchungen.** Berlin: 8°, 2 Teile, 4.20 M.

Frank, M.: **Kaufmännisches Handbuch des Photographen.** Halle a/S, 8 M.

Fröhner, E.: **Lehrbuch der Toxikologie für Tierärzte.** 3 Auflage. Stuttgart, 8°, 391 pp., 9.60 M

Greineder, F.: **Betreibsbuchfuhrung für Gaswerksbetriebe.** München: R. Oldenbourg, 2.60 M.

Grossmann, H., and Neuburger, A.: **Die synthetischen Edelsteine.** Berlin: M. Krayn, 2.50 M.

GRUNWALD, J.: **La technique de l'émaillerie moderne.** Paris: H. Dunod et Pinat, 8°, 4.50 Fr.

GUICHARD, M.: **Manuel de travaux de chimie minerale.** Paris: Hachette & Co., 8°, 7.50 Fr.

HANCKEN, C W.: **Dealin, ein neues Antiseptikum.** Berlin: R. Trenkel, 8°, 36 pp., 2 M.

HEFTER, G.: **Technologie der Fette und Oele.** (4 Bande). **Band III. Die Fettberarbeitenden Industrien I.** Berlin: 8°, 1023 pp., 32 M.

HILLEBRAND, W. F., AND SCHALLER, W.: **The Mercury Minerals from Terlingua, Texas.** W. Wesley, 174 pp., 5 s.

HINTZE, C.: **Handbuch der Mineralogie** Leipzig: Veit & Co., 8°, 5 M.

HOLLEMAN, A. F.: **Lehrbuch der organischen Chemie.** Leipzig: Veit & Co., 8°, 10 M.

Jahrbuch der deutschen Braunkohlen-, Steinkohlen- und Kali-Industrie, 1910. Wilh. Knapp, Halle a/S, 6 M.

Jahrbuch der Radioaktivität und Elektronik. Hrsg. v. Joh. Stark. 7 Bd. I Heft. Leipzig: S. Hirzel, 5 M.

Jahrbuch der technischen Sondergebiete. Herausg. von B. Escales. München: J. F. Lehmann, 6 M.

KAUFFMANN, H.: **Das Radium u. die Erscheinungen der Radioaktivität.** Stuttgart: 8°, 93 pp., 1.40 M.

KAHNERT, P.: **Durchführung des Roheisen-Erz-Prozesses im Martinofen.** Freiberg: Craz & Gelach, 2.50 M.

KAUTNY, T.: **Handb. der autogenen Schweissung.** Halle a/S, 2 Aufl, 5 M.

KIELMEYER, A.: **Der Farberlehrling im Chemie- Examen.** 2 verb. Aufl. Wittenberg: A. Ziemsen, 8°, 289 pp., 6 M.

KIENITZ-GERLOFF, F.: **Botanisch-mikroskopisches Praktikum.** Leipzig: Quelle & Meyer, 8°, 189 pp., 5.60 M.

LANDSBERGER, F.: **Ueber Nitrocumarine und ihre Konstitutionsermittelung.** Berlin: Gustav Heydenreich, 64 pp., 2 M.

LEHMANN, K.: **Die Fabrikation des Surrogatkaffees und des Tafelsenfes.** Wien: A. Hartleben, 8°, 149 pp., 2.80 M.

LEIMBACH, R.: **Die ätherischen Oele. Monographien über chemisch-technische Fabrikationsmethoden.** Band 21. Halle, 8°, 340 pp., 16 M.

LIESS, O.: **Beitrag zur Kenntniss der Wirkung der Formaethrolpräparate.** Leipzig: Otto Nemnich, 33 pp., 1 M.

Luegers Lexicon gesamten Technik. Stuttgart: Deutsche Verlags-Anstalt, 8 Bd., 30 M.

LUFF, A. P., AND CANDY, H. C.: **A Manual of Chemistry, Theoretical and Practical, Inorganic and Organic.** Cassell, 638 pp., 7 s., 6 d.

LUKASZCZYK, J.: **Beiträge zur Erzaufbereitung.** Freiberg: Craz & Gerlach, 2.50 M.

MACAR, J. DE, AND DELATTRE, S.: **Les explosifs militaires violents.** Liége: Ch. Desoer, 8°, 3 Fr.

MASON, W. P.: **Examination of Water (Chemical and Bacteriological).** New York: Wiley & Sons, $1.25.

MEYER, G.: **Chemie und landwirtschaftl. Nebengewerbe.** Zugleich 12 neubearb. Aufl. von Pagels Chemie. Leipzig: Hugo Voigt, 8°, 181 pp., 2 M.

MIE, G.: **Lehrbuch der Elektrizität und des Magnetismus.** Experimentalphysic des Weltäthers für Physiker, Chemiker, Electrotechniker. Stuttgart: 8°, 736 pp., 18.60 M.

MITCHELL, C. A.: **Oil: Animal, Vegetable, Essential and Mineral.** J. Pitman, 8°, 128 pp., 1 s., 6 d.

MOORE, F. J.: **Outlines of Organic Chemistry.** New York: Wiley, 12°, 351 pp., $1.50.

MOSER, A.: **Die elektrolytischen Prozesse der organischen Chemie.** Halle a/S, 10 M.

MULLIKEN, S. P.: **A Method for the Identification of Pure Organic Compounds.** Vol. 3. **Identification of the Commercial Dyestuffs.** New York: Wiley, 8°, 274 pp., $5.00.

MURRAY, J. A.: **Soils and Manures.** London: A. Constable & Co., 8°, 6 s.

NELSON, B. E.: **Introduction to the Analysis of Drugs and Medicines.** New York: Wiley, 12°, 384 pp., $3.00.

OHLMÜLLER, W., AND SPITTA, O.. **Die Untersuchung und Beurteilung des Wassers und des Abwassers.** 3 Aufl. Berlin: 422 pp., 12 M.

OPPENHEIMER, C.: **Grundriss der anorgan. Chemie.** 6 umgearb. Aufl. Leipzig: J. Thieme, 3.50 M.

OSTWALD, W.: **Ueber Katalyse.** Leipzig: (Ann. Naturphilos.), 8°, 1.50 M.

PERKIN, F. M.: **Qualitative Chemical Analysis, Organic and Inorganic.** Third edition. London: Longmans, Green & Co , 8°, 350 pp., 4 s., 6 d.

PERRIN, J.: **Die Brownsche Bewegung u. die wahre Existenz der Moleküle.** Dresden: (Kolloidchem. Hefte), 8°, 84 pp., 2.50 M.

PETERS, H : **Aus pharmazeutischer Vorzeit.** I. Bd., 3 Aufl. Berlin: Julius Springer. 9 M.

PIEK, E.· **Die Oelfeuerung im Schmiedebetrieb und in der Metallwarenfabrikation.** Wien: Akademischer Verlag.

RICHARDS, E. W.: **Laboratory Notes on Industrial Water Analysis.** New York: Wiley & Sons, 50 cents.

RICHARDS, E. H., AND WOODMAN, A. G.: **Air, Water, and Food from a Sanitary Standpoint.** New edition. New York: Wiley & Sons, $2.00.

RICHTER, P.: **Beiträge zur Theorie des Huntington-Heberlein-Prozesses.** Freiberg: Craz & Gerlach, 3 M.

SCHLUNDT, H., AND MOORE, R. B.: **Radioactivity of the Thermal Waters of Yellowstone National Park.** W. Wesley, 8°, 35 pp., 2 s.

SCHMIDT, W.: **Atomauflösung u. elektromotorische Kraft.** Karlsruhe: 8°, 16 pp., 0.50 M.

SCHNEIDEWIND, W.: **Die Kalidüngung.** 3 Aufl. Berlin: Paul Parey, 2 M.

SHARP, J.: **Modern Foundry Practice.** Second edition. New York: Spon & Chamberlain, 8°, 769 pp., $8.00.

SKARK, E. W. L.: **Kurzes Lehrbuch der Chemie für Papiertechniker.** Halle, 8°, 134 pp., 6 M.

SMITH, J. R.: **Modern Assaying.** Philadelphia: Lippincott, 145 pp., $1.50.

STEINHORST, H.: **Studien über Konstitutionsermittelung monohalogenisierter, mono- und dialkylierter Monoketone der Cyclohexanreihe.** Hildesheim: A. Lax, 71, pp., 2 M.

STUTZER, A.: **'Düngerlehre.** 17 Aufl. Leipzig: Hugo Voigt, 2 M.

TAPPEINER, H. v.: **Lehrbuch der Arzneimittellehre und Arzneiverordnungslehre.** Leipzig: F. C. Vogel, 9.25 M.

Taschenbuch für Eisenhüttenleute. Berlin: Wilh. Ernst & Sohn, 15 M.

THOMPSON, C. J. S.: **The Compendium of Medicine and Pharmacy.** Third edition. London: John Bale, Sons and Danielsson.

THOMSON, SIR W. (LORD KELVIN): **Mathematical and Physical Papers: Bd. IV. Hydrodynamics and General Dynamics.** New York: Putnam, 4, 560 pp., $6.40.

VOIGT, M.: **Beiträge zur Oxydation des Phosphors im basischen Konverter.** Freiberg: Craz & Gerlach, 81 pp., 4 M.

VORTMANN, G.: **Uebungsbeispiele aus der quant. chem. Analyse.** 3 Aufl. Wien: Franz Deuticke, 1.50 M.

WALDHEIM, M. v.: **Nach Autoren und Sachnamen geordnete Sammlung der wichtigsten Reagenzien und Reaktionen für Chemie, Pharmazie, Physiologie usw.** 3 Folge. Wien: Franz Deuticke, 102 pp., 2 M.

WALLACH, O.: **Tabellen zur chemischen Analyse.** 4 Aufl. Bonn: Marcus & Weber, 4 M.

WOLK, D.: **Contribution a l'étude de l'azoture d'aluminium et de l'azoture de baryum.** Nancy: Albert Barbier.

Zentralblatt für Chemie und Analyse der hydraulischen Zemente. Halle, 1910-1911 (12 Hefte), 16 M.

ZIMMERMANN, W.: **Moderne Batistfarben.** Zürich: A. Wehner, 5 M.

VOL. XXXII. NOVEMBER, 1910. No. 11.

THE JOURNAL

OF THE

American Chemical Society

EQUILIBRIUM IN THE SYSTEM: POTASSIUM IODIDE, IODINE AND AQUEOUS ALCOHOL.

BY CHARLES L. PARSONS AND H. P. CORLISS.

Received September 14, 1910.

The question of the existence or non-existence of polyiodides of potassium and the various physical and chemical constants of a solution of iodine in potassium iodide has been for years an interesting problem and is still a subject of investigation. Two previous researches upon the subject have been conducted in this laboratory which accomplished little more than to develop the intricacies of the problem and the various precautions necessary to eliminate errors of manipulation and analysis. The question was first attacked in water solution and second in pure alcohol. In both of these the concentration of the solutions became so great near the invariant point (1 liquid and 2 solid phases at the constant temperature 25°) that, at the time, duplication of results could not be depended upon. In pure alcohol, at least, equilibrium in the strongest solutions was reached with extreme slowness and it has since been discovered that filtration through glass wool which was used at the time was inadequate to separate the solid from the liquid phase. As the liquid in these solutions reaches a specific gravity above 3, is absolutely opaque and somewhat viscous, only the most careful filtration can insure the removal of the small solid particles held in suspension which no optical examination will expose.

Since the addition of water to alcohol greatly diminishes the solubility of iodine in the solvent and the addition of alcohol to water likewise affects the solubility of potassium iodide, it was reasoned that by using aqueous alcohol as the solvent, solution of much lower concentrations would be produced at the saturation point and many difficulties thereby eliminated. That this reasoning was incorrect is readily seen from the results that follow, for the degree of saturation when both iodine and potassium iodide are present in the solid phase differs little whether the solvent be water, alcohol or a mixture of the two. Accuracy of analysis was at last attained, however, as results will show, and there is no good reason why the curve can not be traced as well and with equal accuracy in aqueous or alcoholic solution. The problem divides itself into two distinct parts: (*a*) Do polyiodides of potassium exist as solid phases? and (*b*) Do polyiodides exist in solution? The phase rule enables us to give a positive answer to the first part of the problem but unfortunately it has its limitations, and the second query must still remain open to dispute.

Composition of Solid Phases.

As usually happens the literature contains claims for the existence of solid polyiodides of potassium and also evidence of the non-existence at least of the tri-iodide. Johnson[1] states that he succeeded in obtaining lustrous dark blue crystals by evaporating concentrated solutions of iodine in both aqueous and alcoholic potassium iodide, which analysis showed him to be the tri-iodide. As all the mixed crystals obtained from these strong solutions have much the same appearance and can not be separated from the mother liquor, his conclusions are not to be relied upon, especially as analysis is no criterion whatever of the formula of a substance unless its identity as a single compound is proven by other means. The more recent work of Abegg and Hamburger[2] upon solutions of iodine in aqueous potassium iodide is extensive, and they conclude that no polyiodide of potassium exists of less complexity than KI_7. A difference of opinion may be held as to whether the solid phase they analyzed as near to KI_7 was in reality homogeneous. Foote and Chalker[3] give results which, if correct, prove the existence of KI_3 and KI_7. They are in direct opposition to our own and both can not be right. We must leave the judgment to others. We can only suggest that possibly equilibrium was not attained, that the analyses of the solutions supposed to be constant are not in sufficient agreement to prove constancy of composition and that in these concentrated solutions the potassium iodide content of the solid phase, after pressing between filter paper, is alone no real criterion of its true composition. Furthermore, we are unable to plot their results on any semblance to a solubility curve.

In order to study this question a mixture of pure alcohol and pure water containing 60.04 per cent. of alcohol was prepared and saturated with both iodine and potassium iodide in the presence of varying amounts of the other. In order to make doubly certain any results obtained a solution containing 40.03 per cent. of alcohol was treated likewise. The alcohol was carefully freed from aldehydes and ketones. The potassium iodide was J. T. Baker's "special" and was found to be free from iodate and otherwise pure as claimed. The iodine, with the exception of a few of the last experiments, was distilled from water containing potassium iodide, drained, resublimed in dry air and kept for weeks over sulphuric acid before use. In the exceptions noted, our stock being exhausted, a pure resublimed iodine was used and it was proven to have no impurity affecting results by addition to bottles which had already arrived at equilibrium. The potassium iodide was powdered and dried at 180°.

---

[1] *Jour. Chem. Soc.*, 31, 249 (1877).

[2] *Z. anorg. Chem.*, 50, 403 (1906).

[3] *Am. Chem. J.*, 39, 561 (1908).

In order to determine the solubility curves and corresponding solid phases for the system various mixtures were prepared and placed in 100 cc. hard glass bottles, the glass stoppers of which had been carefully ground. The bottles were then rotated in a large thermostat carefully regulated at 25°. The rotating was started December 1, 1909, and the bottles were removed from time to time for analysis and for the addition of more potassium iodide or of iodine as the case might require should examination show that the solid phase had all disappeared.

Equilibrium was reached most quickly in the more concentrated solutions, which was directly contrary to previous experience in pure alcohol. Many of the bottles had not reached equilibrium on March 1st after three months rotation. Practically all were at equilibrium by April 1st, but No. 12 and No. 35 where pure iodine alone was present in solution still showed slight gains on June 1st over analyses made some two weeks previously. They were, however, very near to saturation.

For removing portions of the liquid for analysis a special filter was made, consisting of a glass tube enlarged at the end to hold a platinum disk. This tube was fitted by a ground glass joint to a small pipette and a fine asbestos felt was prepared on the disc, which was washed with alcohol and dried. By drawing through this felt the liquid was absolutely separated from any solid present and the slight diminution in pressure necessary to fill the pipette caused no loss of iodine that could be detected. Many analyses made in duplicate showed that this method could be depended upon to give results varying less than 0.1 per cent. among themselves even in the most concentrated solutions. The liquid so withdrawn was weighed in a glass-stoppered weighing bottle, diluted to 100 cc. with alcohol and aliquot parts taken for analysis. The iodine was determined by titration with an approximately tenth normal thiosulphate solution, carefully standardized against arsenious oxide and pure iodine. The potassium iodide was estimated by careful evaporation in platinum and direct weighing, care being taken to drive off the last traces of iodine by redissolving the residue in water and again evaporating to complete dryness. When equilibrium was reached, as shown by duplicate analyses made many days apart, a portion of the solid phase was removed in a small platinum cup, quickly placed in a weighing bottle and analyzed in like manner. No special attempt to free the solid from mother liquor was made otherwise than to decant off the liquid from the cup before removal from the bottle. Having analyzed the liquid and solid the specific gravity of the liquid was determined in a small Sprengel pycnometer.

The following data are given from which the curves are plotted:

TABLE I.—THE MUTUAL SOLUBILITY OF IODINE AND POTASSIUM IODIDE IN 60 PER CENT. ALCOHOL.

		Analysis of liquid phase.		Analysis of solid phase, together with adhering mother liquor.	
Serial No.	Sp. gr.	Per cent. KI.	Per cent. I.	Per cent. KI.	Per cent. I.
		(a) In equilibrium with excess KI.			
1.........	1.148	30.93	0.0	KI	0.0
2.........	1.191	29.87	4.51	89.13	0.71
3.........	1.285	28.39	12.48	86.60	2.27
4.........	1.368	28.00	18.60	87.30	3.21
5.........	1.427	27.60	21.80	85.75	4.25
6.........	1.533	27.00	28.00	84.39	6.05
7.........	1.776	25.90	40.52	81.05	10.30
8.........	2.250	24.90	52.42	76.21	16.73
9.........	2.507	24.40	58.93	73.20	21.04
10.........	2.845	22.49	65.75	71.66	24.15
11.........	...	21.50	68.95	70.04	26.42
		(b) In equilibrium with excess I.			
12.........	1.134	0.0	23.04[1]	0.0	I
13.........	1.530	7.36	43.05	1.40	88.76
14.........	1.721	10.60	49.38	2.50	88.21
15.........	1.90	12.44	55.33	3.72	87.10
16.........	2.11	13.74	59.26	4.41	86.60
17.........	2.22	15.20	62.66	5.80	85.20
18.........	2.80	17.72	69.10	7.15	85.49
19.........	2.99	19.30	71.90	7.45	88.96
		(c) Invariant point. Excess KI and I.			
20.........	3.162	20.11[2]	72.51	...	...
20.........	Apr. 18	20.03	72.46	21.84	74.64 KI & I
20.........	Apr. 28	20.05	72.54	...	...
20.........	May 6	19.98	72.44	7.40	89.81 I
20.........	May 13	20.08	72.51	20.61	74.09 KI & I
20.........	May 20	20.06	72.44	...	...
20.........	May 23	20.05	72.48	33.46	63.19 KI

Comments on the above table and its graphical representation in Fig. 1 are almost unnecessary. The analyses given are the final ones after equilibrium had been proven. Their accuracy may be judged from the seven analyses given of the most concentrated liquid at the invariant point No. 20. At this point the liquid was shown to be in equilibrium with iodine, with potassium iodide and with two mixtures of iodine and potassium iodide. It was first found to be in equilibrium with two solid phases, which could from the nature of the curve be only iodine and potassium iodide. For the sake of further demonstration the liquid was separated from the solid, pure iodine added and further rotated in the thermostat without change in composition. Potassium iodide was now added and it was later found to be still in equilibrium with this new mixture. It was again separated from the solid and rotated in contact with pure potassium iodide but no change in composition took place. As only two solid phases can co-exist at the invariant point, no polyiodide can be present. It might also be well to call attention to the highest concentration and the interesting fact that a mixture of twenty grams

---

[1] Final analysis June 1, saturation point may not have been quite reached.

[2] Analysis April 12th.

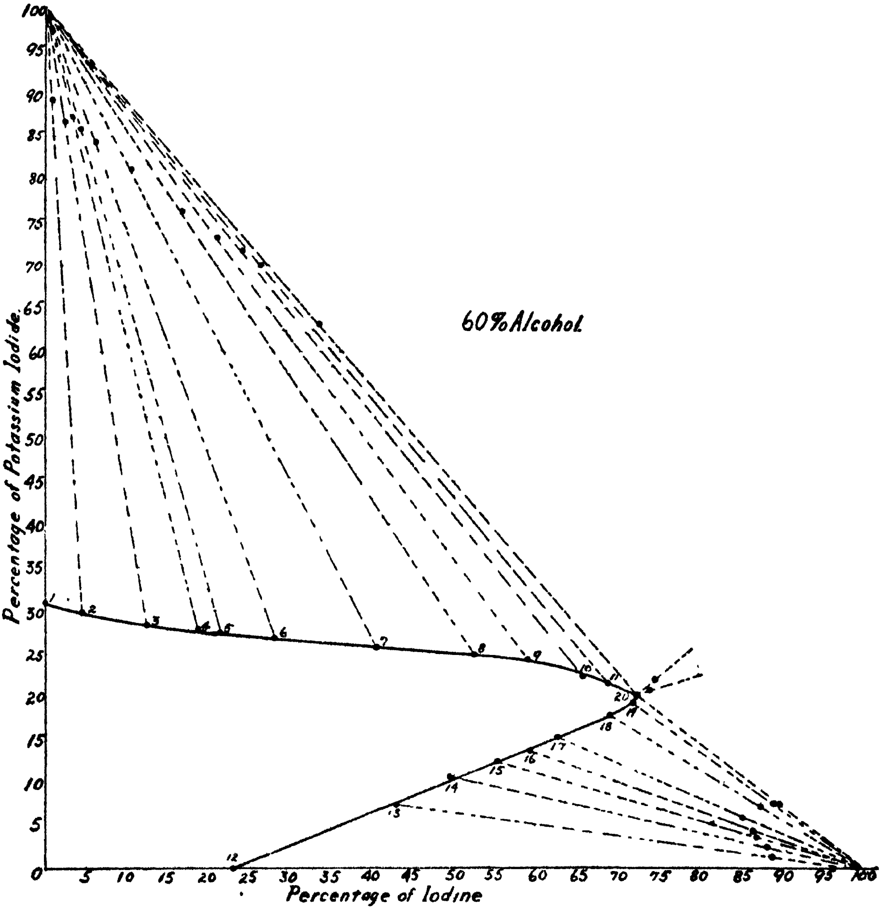


Fig. 1.

of potassium iodide and 72.5 grams of iodine can be kept in solution by 7.5 grams of 60 per cent. alcohol at 25°. Also the mutual solubility of potassium iodide and iodine increases in proportion to the amount of the other present, although the *percentage* composition of the potassium iodide decreases. At the invariant point the liquid phase contains nearly two and one-half mols of iodine for each mol of iodide.

In Fig. 1 are shown the two solubility curves meeting at the invariant point 20. The numbered points represent the composition of the liquid phases and the unnumbered points the solid phases together with adhering mother liquor in equilibrium with them. The extension of the lines joining these points shows the actual composition of the solid phases present.

As before stated, the solubility curves for solution in 40 per cent. alcohol were also determined and their perfect analogy to the 60 per cent. curve are interesting and confirmatory.

The data follow. Again point 35, pure iodine in aqueous alcohol,

TABLE II.—THE MUTUAL SOLUBILITY OF IODINE AND POTASSIUM IODINE IN 40 PER CENT. ALCOHOL.

		Analysis of liquid phase.		Analysis of liquid phase, together with adhering mother liquor.	
Serial No.	Sp. gr.	Per cent. KI.	Per cent. I.	Per cent. KI.	Per cent. I.
		(*a*) In equilibrium with excess KI.			
21	1.339	42.10	0.0	KI	0.0
22	1.377	40.83	3.76	89.21	0.70
23	1.455	38.94	10.09	88.80	1.90
24	1.532	37.41	15.71	88.19	3.02
25	1.605	36.25	20.52	87.04	4.21
26	1.655	35.38	24.44	86.08	5.11
27	1.847	33.26	33.62	83.61	8.41
28	2.024	31.71	39.99	82.06	10.76
29	2.169	30.59	44.76	80.80	12.35
30	2.558	28.56	55.[illegible]	75.90	18.63
31	2.784	26.95	60.27	74.77	20.86
32	...	24.52	65.93	72.98	23.61
33	...	23.04	69.93	72.45	25.04
		(*b*) In equilibrium with excess I.			
35	0.962	0.0	2.97[1]	0.0	I
36	1.292	8.45	28.70	1.85	84.51
37	1.581	12.56	40.63	3.41	84.02
38	...	15.20	49.95	4.98	83.81
39	2.000	16.02	52.95	5.60	82.96
40	2.173	17.18	57.37	6.61	83.60
41	2.749	19.20	66.89	8.45	85.16
42	2.902	20.12	69.10	7.08	88.81
		(*c*) Invariant point. Excess KI and I.			
34	3.246	22.50	70.79	19.48	76.24
34[2]	...	22.43	70.88	69.37	26.14

[1] Final analysis June 1st. Saturation point may not have been quite reached.

[2] After addition of KI and further rotation.

reached equilibrium with extreme slowness and may not be quite saturated after six months' rotation. Point 34 was also shown to be in equilibrium with two different mixtures of two solid phases, but no attempt was made to put it in contact with pure iodine or pure iodide, as the proof was already complete.

The data in Table II are graphically represented on the two solubility curves in Fig. 2, which is drawn on the same principle as Fig. 1.

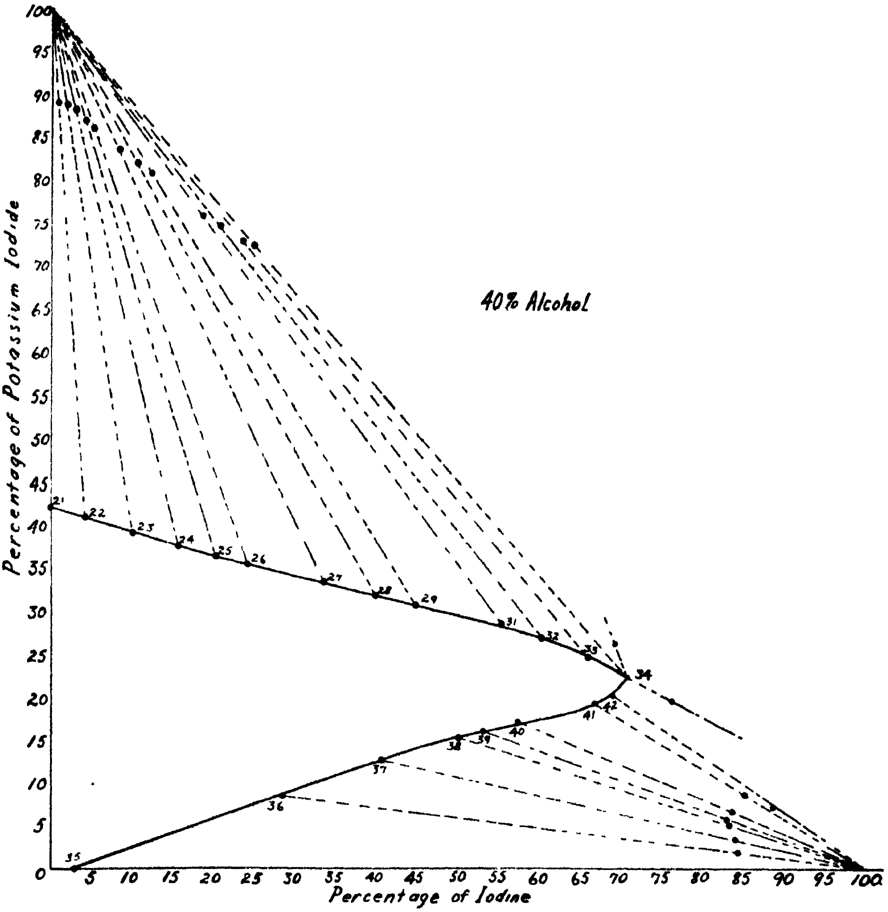


Fig. 2.

Composition of Liquid Phase.

While the non-existence of solid polyiodides of potassium is no proof that they may not exist in solution, it is at least strange that they can not be separated therefrom. Especially is this true when all the evidence in favor of their existence shows that in all solutions of potassium iodide saturated with iodine about one-half of the iodine present must be so combined and that in concentrated solutions the amount of iodine present and unaccounted for as KI_3 is much greater than this proportion. It is not the purpose of this paper to enter into an extended discussion of the problem. From the viewpoint of the dissociation theory, applied to *dilute* solutions, the ground is already well covered in literature, but as the solutions pass above 0.1 normal all formulas obtained begin to lose their force and at higher concentrations do not agree at all with observed facts. While the assumptions made apply well to dilute solutions, they do not show that other assumptions may not explain the conditions equally well, and they all have to discard the mass law as inapplicable as the concentrations increase.

Dossius and Weith[1] early pointed out that strong solutions of iodine in aqueous potassium iodide precipitate iodine on dilution, which is contrary to the mass law if the iodine is present as tri-iodide. LeBlanc and Noyes[2] explain the rise of the freezing point and the decrease in the conductivity when iodine is dissolved in aqueous potassium iodide by assuming the formation of polyiodides. Jakowkin[3] by experiments on the distribution of iodine between aqueous potassium iodide and carbon disulphide developed a mass law constant for dilute solutions indicating that potassium tri-iodide was present and was the only polyiodide present in any amount. His conclusions were based on the relative solubility of iodine in pure water and in carbon disulphide, assuming the potassium iodide present to have no simple solvent effect on the iodine. Dawson,[4] Burgess and Chapman[5] and Laurie[6] have also studied the matter from a similar standpoint and from considerations of transference and electromotive force. In dilute solutions they are in fair agreement. One of us[7] has already pointed out that the conclusions of Jakowkin, upon which most of the subsequent work is either grounded or to which the results obtained are compared, are untenable if dissolved potassium iodide itself has a simple solvent action for iodine such as added alcohol or acetic acid would possess. Furthermore, it was shown that these solutions of iodine in aqueous potassium iodide were perfectly analogous in their osmotic and conductance properties to such ternary mixtures as camphor in aqueous acetic acid and, osmotically at least, to all ternary mixtures where one of the dissolved substances was rendered less soluble by dilution of the mixture with that component which separated out first

[1] *Z. Chem.*, 1869, 379.

[2] *Z. physik. Chem.*, 6, 401 (1890).

[3] *Ibid.*, 20, 36 (1896).

[4] *J. Chem. Soc.*, 79, 239 (1901); 81, 524; 93, 1308, 2063.

[5] *Ibid.*, 85, 1305.

[6] *Z. physik. Chem.*, 64, 615; 67, 627.

[7] Parsons, *J. Physic. Chem.*, 11, 669 (1907).

on freezing. Indeed it was definitely pointed out that Miller[1] had thermodynamically shown that in all such binary solvents the freezing point must of necessity rise on addition of the third component. Accordingly, the assumption of complexes was not necessary to qualitatively explain the facts. Many published instances were cited of such ternary mixtures where the same reasoning as is applied to the demonstration of the polyiodides would lead to incomprehensible complexes. Bray and McKay,[2] on the assumption that the decrease in conductivity on dissolving iodine in dilute aqueous potassium iodide is due solely to the formation of KI_3, arrive at results in excellent agreement with those of Burgess and Chapman which they believe prove the existence of this polyiodide. They have also attempted to account for the abnormalities in concentrated solutions and find that the deviations from the mass law are not very serious below 0.1 normal potassium iodide but still are not negligible even below this concentration. While admitting the character and force of their arguments, especially when viewed from their standpoint, it should not be forgotten that similar reasoning would probably lead to poly-camphor compounds of acetic acid and other equally improbable complexes wherever the conductivity is diminished by adding a solute to a binary solvent. Furthermore, these results, and the results of the other authorities mentioned are applicable, without other assumption, only to that very limited portion of the solubility curve, which is less than tenth-normal. This is the only portion of the curve where the actual iodine solubility is equivalent in mols to one-half the iodide present and quantitatively meets the theory of Jakowkin. It appears to the authors of this paper that the phenomena accompanying mixtures of potassium iodide, iodine and water (or alcohol) are much more analogous to those known to apply to some ternary alloy mixtures than they are to the properties of known complexes such as some of the double cyanides.

In the paper by one of us[3] already cited it was shown that while known complexes such as potassium silver cyanide, potassium ferrocyanide, etc., pass through a membrane as such without decomposition, such was not the case with hypothetical potassium tri-iodide, which was shown to behave similarly to certain double salts like the alums that are supposed to exist as simple molecules in solution. Exception having been taken to these experiments on the basis that the solutions used were too concentrated, containing more iodine than any conception previously advanced could account for, and also that a membrane was an unknown quantity in dialysis, it was decided to attack the matter again, using sufficiently dilute solutions to carry conviction to all and agar-agar jelly in place of a membrane. Agar-agar was chosen because it has been shown to offer little, if any, resistance to electrolytes while allowing true diffusion phenomena to take place unaffected by convection currents. The experimental work was conducted, under the supervision of one of us, by Mr. George A. Perley, to whom our acknowledgments are due.

---

[1] *J. Physic Chem.*, 3, 160.

[2] *J. Am. Chem. Soc.*, 32, 914.

[3] *J. Physic. Chem.*, 11, 659 (1907).

Cylinders closed at one end were made of 3 per cent. agar jelly, using 0.1 normal potassium iodide as solvent. They resembled tall beakers, having walls approximately eleven millimeters thick. They were kept immersed in 0.1 normal potassium iodide until needed. When in use these cylinders were placed in 400 cc. Jena beakers containing 200 cc. 0.1 normal potassium iodide and were then filled nearly full with the iodine-saturated potassium iodide solution employed in the particular experiment and the whole placed in a thermostat at 25°. All the solutions had previously been brought to this temperature, the level of the liquids within and without the cylinder was kept the same and both liquids were mechanically stirred by plungers throughout the experiment.

According to Jakowkin's researches and the theory of those who believe in the presence of polyiodides, a solution of potassium iodide saturated with iodine must have one-half of the potassium iodide converted into tri-iodide and contain also a small, almost neglible amount of iodine dissolved as such in the water present.

In the first experiment tried the outer solution was 0.1 normal potassium iodide and the inner solution was 0.16 molar potassium iodide saturated with iodine.

According to Jakowkin the following conditions should exist and the potassium iodide should, of course, diffuse from higher to lower concentration or from left to right.

Outer solution.	Inner solution.
	0.08 molar KI
0.1 molar KI	0.08 molar KI_3
	0.0013 molar I_2

If there is no complex present, the following conditions should exist and potassium iodide should diffuse from right to left.

Outer solution.	Inner solution
0.1 molar KI	0.16 molar KI
	0.0813 molar I_2

At stated periods the outer liquid was removed for analysis and replaced by a fresh portion of 200 cc. each. The first portion was taken off just as the iodine diffused to the outer wall. This took almost exactly two hours and was easily judged by the eye. It will be seen at once that the potassium iodide passed outward and that a notable portion had passed through ahead of any iodine as was to be expected from its smaller molecular weight. The following results were obtained:

Analysis of outer solution after diffusion showing a total gain in outer solution for each 200 cc. and each period:

Period.	Time.	M. mols I_2.	M. mols KI.
1	2	trace	0.876
2	12	2.951	5.26
3	12	2.355	5.75
4	12	1.475	5.46

As a check, the same experiment was performed using simply the 0.1 molar and 0.16 molar potassium iodide solutions without added iodine. Considering the fact that different cylinders of agar-agar were used and that no attempt was made to accurately adjust the height of the liquid to the same diffusing surface as before the results are quite comparative.

GAIN OF KI IN OUTER SOLUTION.

Period.	Time.	M. mols KI.
1	2	1.84
2	12	6.501
3	12	5.64
4	12	5.45

In a second experiment it was decided to use 0.1 molar potassium iodide as the outer solution and a 0.1 molar potassium iodide inner solution saturated with iodine.

According to Jakowkin the following conditions would exist and the solution should therefore pass from left to right:

Outer solution.	Inner solution.
0.1 molar KI	0.05 molar KI 0.05 molar KI_3 0.0013 molar I_2

If no complex exists, then

Outer solution.	Inner solution.
0.1 molar KI	0.10 molar KI 0.0513 molar I_2

Here again the results of experiments are against the conception of any complex being present as the following show:

ANALYSIS OF OUTER SOLUTIONS OF 200 CC. EACH SHOWING TOTAL GAIN.

No.	Time.	M. mols I.	M. mols KI.
1	12	0.889	none
2	13	1.58	none

Analyses of the two portions of outer solution used showed them to be unchanged in their potassium iodide concentration.

In the above analyses the free iodine was titrated with thiosulphate and the total iodine was determined in a separate portion, being set free by ferrous chloride and sulphuric acid and distilled into a solution of potassium iodide, using an apparatus consisting entirely of glass. Many check analyses were run showing the agar to be without effect on the analytical results. Also the experiments were repeated with results entirely in accord with those cited.

We believe the above results strongly indicate that no polyiodide exists to any notable extent in these solutions and that we have here simply a case of "solution in a dissolved solid,"[1] a solid which above 82° has been shown by Abegg and Hamburger[2] to be itself a remarkable solvent for iodine. We have already pointed out that its behavior in regard to rise in freezing point, decrease in conductivity and distribution phenomena, upon which all claims to complexes in solution are based, have interesting analogies to many ternary mixtures where no such combination would be claimed. The idea of simple solution in a binary solvent has the added advantage that it explains the phenomena of the concentrated solutions equally well with those which are more dilute.

Summary.

No polyiodides of potassium exist as solid phases at 25°.

Potassium iodide and iodine, placed together in aqueous solution, apparently diffuse independently of any chemical combination with each other. Judging from this standpoint alone no polyiodide of potassium is present in solution.

NEW HAMPSHIRE COLLEGE,
DURHAM, N. H.

DIFFUSION PHENOMENA OF THE ALUMS.

BY CHARLES L. PARSONS AND W. W. EVANS.

Received September 14, 1910.

In connection with the diffusion experiments on solutions of iodine in potassium iodide described in the preceding paper and those on known complexes reported in a previous paper by one of us,[3] it seemed desirable to make preparatory trials on crystal complexes which were known or supposed to exist as a mixture of simpler molecules when dissolved. For this purpose ordinary alum was chosen and the work proved so interesting that the experiments were extended to other alums and were performed at 0° and 25°. This paper is written for the purpose of putting these data on record for the different alums studied. Its conclusions are simply confirmatory of previous work.

---

[1] To explain what is meant by solution in a dissolved solid it may be pointed out that so far as analogy goes the only difference between dissolving potassium iodide in water and water in alcohol is that one is a solid and the other a liquid at the temperature at which most of our ordinary ideas are conceived. Sugar is not soluble in alcohol until water is added, but it is doubtful if any one would claim that the solubility of sugar in aqueous alcohol is due to the formation of sugar hydrates. It is simply because sugar is soluble in water and if one worked at —1° it would be a solid we were adding which, after dissolving, in its turn dissolved the sugar. In like manner working at 15° solid acetic acid dissolving in water acts as a solvent for camphor and the latter gives analogous conditions as to *rise* in freezing point and *decrease* in conductivity to those that exist when iodine, itself practically insoluble in water, is brought easily into solution when dissolved potassium iodide is present.

[2] *Z. anorg. Chem.*, 50, 403 (1906).

[3] Parsons, *J. Physic. Chem.*, 11, 659 (1907).

The alums while crystallizing as complex molecules have long been known to exist as simple sulphates when dissolved. Some early diffusion experiments by Graham[1] were the first to show that the two sulphates of which ordinary alum is composed can be separated by diffusion. This was later confirmed by Marignac,[2] who came to the conclusion that double salts like the alums are found only at the moment of crystallization. Later Rudorff, using goldbeater's skin as a separating membrane,[3] reached much the same conclusion. Gerlach[4] points out that certain slight volume changes that took place when he mixed solutions of the constituents of the alums indicated the combination of these constituents but his arguments are not convincing when the evidence to the contrary is considered. Besides the above authorities, who argued from a diffusion standpoint, a number of investigations have been undertaken on the cryoscopic and conductivity constants of the alums, of which the research by Jones and Mackay[5] is perhaps the most complete. They likewise reach the conclusion that the alums exist for the main part only in the solid condition, although they found some evidence that as the solutions grew more concentrated there may have been some association in solution.

In our experiments a known amount of solution was placed either in parchment tubing, which is permeable to the simple constituents of the alums, or in cylinders of agar-agar jelly. These were then placed in beakers containing a measured amount of water and both inner and outer solutions constantly stirred in a thermostat for the periods of time stated below.

The solutions were analyzed by well-known methods and carefully checked. The method used to determine chromium while using well-known principles we did not find described elsewhere. A measured amount of the chromium solution was diluted to about 150 cc. with water, and about 1 gram sodium peroxide was added, the solution was heated and allowed to boil for about ten minutes, then cooled somewhat and diluted to about 400 cc. Then the solution was acidified with 5 cc. of sulphuric acid (1 : 1), 2 grams of potassium iodide were added and the liberated iodine was titrated in the usual manner with a standard solution of sodium thiosulphate. In every case good duplicates could be obtained.

---

[1] *Ann. Chem. Pharm.*, 17, 56 (1851).

[2] *Ann. chim. phys.* [5], 2, 546 (1874).

[3] *Ber.*, 21, 4 (1888).

[4] *Z. anal. Chem.*, 28, 485.

[5] *Am. Chem. J.*, 19, 83 (1897).

Diffusion of Ammonium Chrome Alum.

The outside solution in each case was 200 cc. water. The experiment was conducted at 25°, each portion being run for three hours. The inside solution contained in 50 cc. the alum equivalent to 3.268 grams $Cr_2(SO_4)_3$ and 1.100 grams $(NH_4)_2SO_4$, the ratio of mols of each being 1 : 1. Parchment tubing was used.

COMPOSITION OF DIFFUSATE.

Period.	M. mols $(NH_4)_2SO_4$.	M. mols $Cr_2(SO_4)_3$.	$\frac{(NH_4)_2SO_4}{Cr_2(SO_4)_3}$.
1	5.6	1.228	4.48
2	2.4	1.200	2.00
3	1.2	0.848	1.41
4	0.36	0.6928	0.520
Inside solution after completion of experiment.	0.038	0.416	0.091

From the above it can be seen that there is an almost complete separation of the constituents of the alum into its components.

Diffusion of Potassium Chrome Alum.

The inside solution contained in 50 cc. the alum equivalent to 1.459 grams potassium sulphate and 3.278 grams chromium sulphate, the molar ratio being 1 : 1. The experiment was run as in the previous case, the periods being three hours each and the outside liquid consisting of 200 cc. of water at 25°.

COMPOSITION OF DIFFUSATE.

Period.	M. mols K_2SO_4.	M mols $Cr_2(SO_4)_3$.	$\frac{K_2SO_4}{Cr_2(SO_4)_3}$.
1	5.68	1.40	4.06
2	2.25	1.20	1.87
3	0.803	0.864	0.929
4	0.271	0.746	0.363
Solution in membrane after completion of experiment.	0.0688	1.012	0.068

It can be seen that the same separation takes place as in the previous case.

Diffusion of Potassium Aluminium Alum.

Inside solution contained in 50 cc. alum equivalent to 1.455 grams potassium sulphate and 2.856 grams aluminium sulphate, molar ratio 1 : 1. Details the same as in previous cases.

COMPOSITION OF DIFFUSATE.

Period.	M. mols K_2SO_4.	M. mols $Al_2(SO_4)_3$.	$\frac{K_2SO_4}{Al_2(SO_4)_3}$.
1	5.71	1.28	4.46
2	2.05	0.958	2.14
3	0.775	0.855	0.906
4	0.247	0.606	0.408
Solution in membrane after completion of experiment.	0.1049	0.1145	0.916

Diffusion of Ammonium Aluminium Alum.

Inside solution contained in 50 cc. the alum equivalent to 1.1014 grams ammonium sulphate and 2.852 grams aluminium sulphate, molar ratio 1 : 1. Details same as in previous cases.

COMPOSITION OF DIFFUSATE

Period.	M mols $(NH_4)_2SO_4$.	M. mols $Al_2(SO_4)_3$	$\frac{(NH_4)_2SO_4}{Al_2(SO_4)_3}$.
1	5.6	3.52	1.59
2	1.85	0.696	2.80
3	0.70	0.571	1.22
4	0.50	0.875	0.58
Solution in membrane after completion of experiment.			
	0.35	0.355	0.98

There was probably some error which entered in the first period, as can be seen from the ratio.

Diffusion of Ferric Ammonium Alum.

The inside solution was made up so that 50 cc. contained the alum equivalent to 1.103 grams ammonium sulphate and 3.334 grams ferric sulphate, molar ratio being 1 : 1. Details same as in previous cases.

COMPOSITION OF DIFFUSATE.

Period	M mols $(NH_4)_2SO_4$	M mols $Fe_2(SO_4)_3$	$\frac{(NH_4)_2SO_4}{Fe_2(SO_4)_3}$.
1	5.12	2.93	1.74
2	3.24	2.54	1.27
3	0.560	1.78	0.315
4	0.160	0.622	0.257
Solution in membrane after conclusion of experiment			
	0.160	0.570	0.287

It was found that in this case there was a tendency on the part of the iron toward hydrolysis, heightened by the removal of the ammonium sulphate. This interfered with the diffusion through the membrane and therefore this separation is not so perfect as in the case of the other alums. However, as can be seen from the above, there is no doubt that separation takes place.

Diffusion at Low Temperature.

Experiments were also conducted in a mixture of snow and water, the temperature being close to 0°, to see what effect a decrease in temperature would have upon the results. In other respects the work was carried on as before.

Diffusion of Ammonium Chrome Alum.

Inside solution same as before, 50 cc. containing the alum equivalent to 1.100 grams ammonium sulphate and 3.268 grams chromium sulphate, molar ratio 1 : 1. The temperature was kept constant by the use of a snow water mixture. Time of each period three hours. Parchment tubing used.

COMPOSITION OF DIFFUSATE.

Period.	M. mols $(NH_4)_2SO_4$.	M. mols $Cr_2(SO_4)_3$.	$\frac{(NH_4)_2SO_4}{Cr_2(SO_4)_3}$.
1	3.60	0.552	6.52
2	2.20	0.520	4.44
3	1.24	0.453	2.74
4	0.88	0.426	2.06
Solution left in membrane after close of experiment.			
	0.187	1.83	0.0122

Diffusion of Potassium Chrome Alum.

Inside solution as before, 50 cc. containing an amount of the alum equivalent to 1.459 grams potassium sulphate and 3.278 grams chromium sulphate, molar ratio 1:1. Details as above.

COMPOSITION OF DIFFUSATE.

Period.	M mols K_2SO_4.	M. mols $Cr_2(SO_4)_3$.	$\frac{K_2SO_4}{Cr_2(SO_4)_3}$.
1	3.80	0.880	4.32
2	2.50	0.506	4 94
3	0.736	0.466	1.59
4	0.665	0.440	1 50
Solution in membrane after conclusion of experiment.			
	0.0143	2 075	0.007

From the above work it can be seen that there is a separation at 0° as well as at 25°. The molecules at this temperature move more slowly as one would expect; consequently the separation of the two is not so rapid as at higher temperatures, but it is more complete.

Diffusion through Agar Jelly.

Graham has shown[1] in working with agar-agar jelly that mixtures of salts diffuse readily from aqueous solutions and that the diffusion constants do not change with rise of temperature but the amount of diffused salt regularly increases. He found that the rate of diffusion is practically the same for different concentrations of the jelly.

For our experiments a cylinder of the jelly closed at one end was made from a 3 per cent. solution, having walls about 11 mm. thick. The alum solution was placed inside and allowed to diffuse out into 150 cc. of water. The temperature was kept at 25° throughout the experiments. Each portion was run for a period of 24 hours and the portions analyzed.

Diffusion of Ammonium Chrome Alum.

The solutions used were the same as in the previous work. Periods 24 hours each.

---

[1] *J. Chem. Soc.*, 56, 816.

Composition of Diffusate.

Period.	M. mols $(NH_4)_2SO_4$.	M mols $Cr_2(SO_4)_3$.	$\frac{(NH_4)_2SO_4}{Cr_2(SO_4)_3}$.
1	2.28	0.426	5.35
2	1.26	0.810	1.55
3	0.90	0.720	1.25
Solution in cell after conclusion of experiment.			
	0 05	0.13	0.039

Diffusion of Ammonium Aluminium Alum.

Solutions same as previously used. Periods 24 hours each.

Composition of Diffusate.

Period.	M. mols $(NH_4)_2SO_4$.	M. mols $Al_2(SO_4)_3$.	$\frac{(NH_4)_2SO_4}{Al_2(SO_4)_3}$.
1	1.62	0.585	2.77
2	1.26	0.792	1.28
Solution in cell after conclusion of experiment.			
	0.70	0.138	0 507

The results of these experiments with agar-agar show in the same way as with parchment that the constituents of the alums diffuse independently.

Conclusions.

When alums are dissolved in water they are decomposed into the simple sulphates, which can be separated from each other by diffusion. The chrome alums separate more readily than the aluminium alums. This is in entire accord with previous researches.

THE SOLUBILITY OF BARIUM NITRATE AND BARIUM HYDROXIDE IN THE PRESENCE OF EACH OTHER.

By C. L. Parsons and H. P. Corson.

Received September 14, 1910.

The work of Cameron and Robinson upon the system lime, nitric acid and water[1] proves the existence of a basic nitrate of calcium having a composition represented by $2CaO.N_2O_5.3\frac{1}{2}H_2O$. Their work suggested the possibility of the existence of similar compounds of barium, but in a careful search of the literature we were unable to find any record of such work upon barium. Hence the present investigation was undertaken.

A specially prepared barium nitrate obtained for this research was carefully tested for impurities. The salt was found to be very pure, no foreign substance being detected except a small amount of carbonate. A saturated solution of the nitrate was prepared and made slightly, yet distinctly, acid with nitric acid and boiled to remove carbon dioxide.

The barium hydroxide obtained for the work was found to be quite pure except for the presence of carbonate, which was eliminated by filtering a hot concentrated solution with careful exclusion of the carbon dioxide of the air. Upon cooling this solution, crystals of pure hydroxide separated out. This solid was dipped out with adhering solution and added to the solutions of nitrate.

---

[1] *J. Physic. Chem.*, **2**, 273 (1907).

Bottles were made up in regular steps of concentration from pure water to a saturated solution of barium nitrate, using freshly boiled distilled water for dilution. Barium hydroxide was then added until sufficient solid persisted. One bottle also had excess of solid nitrate added and two were made alkaline with barium hydroxide, but short of saturation, and excess of solid nitrate added. The bottles were sealed and constantly rotated in a water thermostat maintained at 25° until equilibrium was reached. The bottles were not opened for four months, although equilibrium was undoubtedly complete much earlier, since no reaction occurred and subsequent analysis of all bottles showed no change.

Previous experiment had shown that the gravimetric estimation of barium could be made more accurately in these pure salt solutions by weighing barium nitrate than by the usual sulphate method. Consequently the *total* barium oxide present was determined by this method. Portions of the solutions amounting to about 5 cc. were drawn off and weighed in a weighing bottle, transferred to a platinum dish, acidified with nitric acid and evaporated in an air bath at 100°. After the solution had come down to dryness, the temperature was increased to 115° to remove the last traces of free acid and moisture. The samples were then cooled and weighed as barium nitrate.

Barium oxide present as *hydroxide* was determined volumetrically by titrating a weighed portion of the solution with tenth normal nitric acid, using phenolphthalein as indicator.

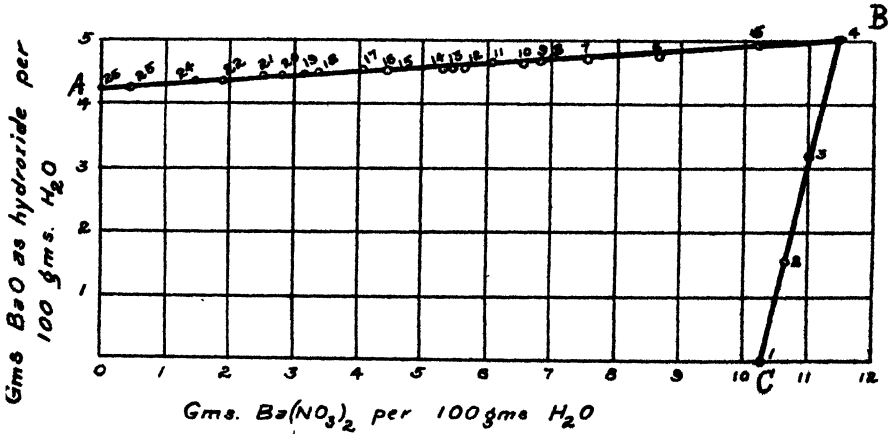


Fig. 1.

The data obtained are given in Table I, which shows (Nos. 4–26) the solubility of barium hydroxide in solutions of barium nitrate of various concentrations and (Nos. 1–4) the solubility of barium nitrate in solutions of barium hydroxide. No. 4 represents the composition at the invariant point where both solids are present in excess.

The results are expressed graphically in Fig. 1.

From an inspection of this chart, it will be seen that there are two distinct branches, AB and BC, to the isotherm. As this is a three-component system, along each of these two branches there can be only one solid phase in equilibrium with the solution.

TABLE I.

Serial No.	Density 25°/25°.	Grams BaO as $Ba(OH)_2$ in 100 H_2O.	Grams $Ba(NO_3)_2$ in 100 H_2O.
1	1.0797	none	10.30
2	1.1002	1.55	10.66
3	1.1210	3.22	11.04
4	1.1448	5.02	11.48
5	1.1371	4.93	10.21
6	1.1288	4.83	8.66
7	1.1220	4.72	7.55
8	1.1133	4.72	7.01
9	1.1062	4.65	6.82
10	1.1044	4.61	6.55
11	1.1010	4.64	6.08
12	1.0975	4.60	5.66
13	1.0949	4.55	5.46
14	1.0937	4.54	5.32
15	1.0885	4.52	4.44
16	1.0864	4.53	4.41
17	1.0840	4.52	4.04
18	1.0790	4.48	3.47
19	1.0774	4.46	3.14
20	1.0731	4.40	2.79
21	1.0711	4.42	2.53
22	1.0651	4.35	1.88
23	1.0626	....	....
24	1.0640	4.35	1.45
25	1.0538	4.29	0.43
26	1.0512	4.29	none

Several of the solids in contact with the solutions were analyzed. Along branch BC of the curve (Fig. 1) the solids were dipped from the solutions with a platinum spoon, no attempt being made to free them from mother liquor save by decantation. They were analyzed in exactly the same manner as the liquids, namely, titration of a weighed portion with nitric acid, then evaporation and weighing as nitrate.

The solids along branch AB of the curve (Fig. 1) were pure hydroxide and when pressed between filter paper contained so small a quantity of N_2O_5 that it was not practical to determine the exact amount. Table II gives the percentage composition of all the solutions, together with some of the corresponding residues.

TABLE II.

No.	Solutions.			Residues with adhering solution.		
	BaO. Per cent.	N_2O_5 Per cent.	H_2O. Per cent.	BaO. Per cent.	N_2O_5. Per cent.	H_2O. Per cent.
1	5.48	4.86	89.66	50.21	35.38	14.41
2	6.95	3.92	89.13	51.44	36.22	12.34
3	8.46	3.98	87.56	50.29	35.12	14.59
4	10.05	4.06	85.89	56.44	35.20	8.36
5	9.43	3.63	86.94	.....	.....	.....
6	8.80	3.21	87.99	.....	.....	.....
7	8.12	2.78	89.10	.....	.....	.....
8	7.94	2.64	89.42	.....	.....	.....
9	7.72	2.52	89.76	.....	.....	.....
10	7.57	2.42	90.01	.....	.....	.....
11	7.38	2.26	90.56	.....	.....	.....
12	7.15	2.11	90.74	.....	.....	.....
13	7.01	2.04	90.95	.....	.....	.....
14	6.92	1.98	91.10	.....	.....	.....
15	6.57	1.71	91.72	.....	.....	.....
16	6.50	1.66	91.84	.....	.....	.....
17	6.32	1.54	92.14	.....	.....	.....
18	5.96	1.29	92.75	.....	.....	.....
19	5.83	1.20	92.97	.....	.....	.....
20	5.65	1.08	93 27	.....	.....	.....
21	5.49	0.97	93.54	.....	.....	.....
22	5.13	0.74	94.13	.....	.....	.....
23	4.88	0.56	94.54	.....	.....	.....
24	4.92	0.58	94.50	.....	.....	.....
25	4.32	0.17	95.51	.....	.....	.....
26	4.10	none	95.90	.....	.....	.....

Along the other branch, BC of the curve, the composition of the solid, evidently the nitrate, was proved by plotting the results of analyses on a triangular diagram.[1] When plotted in this manner the lines connecting the points representing liquids with other points representing their corresponding solids meet in a point which as scaled off on the diagram has the composition BaO 58.7, N_2O_5 41.3. This solid, then, is represented by the formula $BaO.N_2O_5$. The analysis of the solid in bottle No. 4, which lies at the intersection of the two branches of the isotherm, shows, of course, that it consists of both $Ba(OH)_2.8H_2O$ and $Ba(NO_3)_2$. Examination of the residues by the microscope is entirely in agreement with the conclusions arrived at by analysis.

---

[1] Schreinemakers, *Z. physik. Chem.*, 11, 81 (1893); Bancroft, *J. Physic. Chem.*, 6, 181 (1902).

Conclusions.

The solubility of barium hydroxide in solutions of barium nitrate increases as the concentration of the latter increases. This fact is interesting, for in most cases a common ion tends to decrease the solubility of substances in solution in a common solvent.

The solid in equilibrium with any solution along curve AB, Fig. 1, is $Ba(OH)_2.8H_2O$, and along curve BC, is $Ba(NO_3)_2$.

Consequently, we conclude that basic nitrates of barium do not exist at 25°.

NEW HAMPSHIRE COLLEGE,
DURHAM, N. H.

THE SOLUBILITY OF STRONTIUM NITRATE AND STRONTIUM HYDROXIDE IN THE PRESENCE OF EACH OTHER.

BY C. L. PARSONS AND C. L. PERKINS.

Received September 14, 1910.

In connection with the work described in the preceding paper on the solubility of barium nitrate in solutions of barium hydroxide it was decided to make a similar study of the strontium compounds and for the same reason. No basic nitrates of strontium have been described in the literature, but there was no certainty that a search along equilibrium lines might not reveal them.

A specially pure lot of strontium nitrate was prepared by separating the barium from a salt purchased as pure and containing no other contamination. Strontium hydroxide was prepared from pure strontium oxide by dissolving it in boiling water and filtering hot. Upon cooling the solution strontium hydroxide crystallized out and was preserved under the mother liquor. It was protected from the formation of carbonate by a sodium hydroxide seal.

A saturated solution of the nitrate was prepared and boiled with a slight excess of nitric acid to assure the absence of all carbonates. From this a series of solutions was made by diluting with freshly boiled, distilled water in varying amounts and adding the solid hydroxide until a solid phase persisted in sufficient quantity for analysis. One bottle also had excess of solid nitrate added and two bottles similarly prepared were made to contain hydroxide short of saturation. The solutions were placed in tightly stoppered bottles, the glass stoppers of which had been carefully ground, and rotated in a thermostat kept at 25° for more than a month before any analyses were made. Subsequent trials proved that equilibrium had already been attained.

Previous experimentation having shown that the methods used for barium in the research already referred to were applicable here, they were, accordingly, used. Definite portions of the solution were drawn off, weighed, acidified with nitric acid, evaporated to complete dryness and the total strontium nitrate weighed as such. The hydroxide present was determined by titrating a separate portion with tenth normal nitric acid.

The data obtained are given in Table I, which (Nos. 1–22) shows the solubility of strontium hydroxide in solutions of strontium nitrate of various concentration; also (Nos. 24–25) the solubility of strontium nitrate in varying solutions of strontium hydroxide. No. 2 indicates the conditions that exist at the invariant point when the solution is saturated with both substances.

Table I.

Bottle No.	Sp. gr. 25/25.	SrO as $Sr(OH)_2$ in 100 grams H_2O.	$Sr(NO_3)_2$ in 100 grams H_2O.
1	1.481	0.0	79.27
2	1.506	1.76	81.06
3	1.490	1.71	74.27
4	1.450	1.55	66.88
5	1.419	1.51	63.71
6	1.403	1.47	60.37
7	1.381	1.41	56.30
8	1.359	1.34	52.90
9	1.327	1.27	46.97
10	1.317	1.20	44.03
11	1.291	1.14	40.83
12	1.267	1.11	37.81
13	1.239	1.03	32.41
14	1.217	1.01	28.80
15	1.206	0.96	26.58
16	1.178	0.95	23.83
17	1.148	0.91	17.96
18	1.126	0.87	16.21
19	1.108	0.84	12.78
20	1.079	0.81	8.96
21	1.059	0.79	6.29
22	1.033	0.78	4.45
24	1.492	0.38	79.47
25	1.494	0.78	80.83

The results are expressed graphically in Fig. 1.

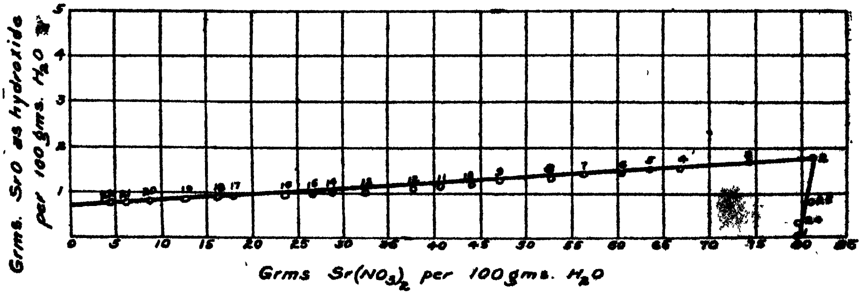


Fig. 1.

From an inspection of this chart it will be seen that there are only two distinct branches to the isotherm. As this is a three-component system, along each of these two branches there can be only one solid phase in equilibrium with the solution. Reference to the curve shows that the presence of either component increases the solubility of the other.

This curve in itself is sufficient to indicate the absence of any basic nitrate of strontium, since the composition of the solution varies with regularity. The precipitates were, however, examined through a microscope and several of them were analyzed. The microscope showed the crystals upon the first branch of the curve to be simply those of strontium hydroxide, while those upon the second branch were obviously strontium nitrate.

The analysis of the solids with adhering mother liquor was made as follows: The precipitate was spooned out in quantity sufficient for analysis, the adhering mother liquor was removed as completely as possible by pressing between filter papers and the solid was immediately placed in a closed weighing bottle and weighed. The alkalinity was determined by titrating with standard nitric acid. The total strontium was obtained as in the analysis of the solutions, by evaporation with slight excess of nitric acid. The composition of the solids analyzed together with that of the corresponding solutions is given in Table II.

TABLE II.

	Solution.		Solid	
Bottle No.	Per cent. SrO.	Per cent. N_2O_5.	Per cent. SrO.	Per cent N_2O_5.
3	21.65	21.52	37 86	1.65
8	17.66	17.49	38 61	0.56
19	6.27	5 76	38.92	0.19
24	21.86	22.54	36.50	38 00
25	22.02	22.70	36.98	38 48

An examination of these figures shows them to be entirely confirmatory of the solubility curve and that the only two solids present are $Sr(OH)_2$.-$8H_2O$ and $Sr(NO_3)_2$.

Conclusions.

The solubility of strontium hydroxide in solutions of strontium nitrate increases as the concentration of the latter increases. The curve is similar in form to the curve for barium, but the solubility of the nitrate is much greater and the hydroxide much less than that of the corresponding barium salts.

The solid in equilibrium with any solution on the longer arm of the curve is $Sr(OH)_2.8H_2O$, while along the short arm it is $Sr(NO_3)_2$.

No basic nitrates of strontium exist at 25°.

NEW HAMPSHIRE COLLEGE,
DURHAM, N. H.

THE BINARY AND TERNARY ALLOYS OF CADMIUM, BISMUTH AND LEAD.

BY WILLIAM EDWARD BARLOW.

Received August 10, 1910.

The ternary and quaternary alloys of lead, bismuth, cadmium and tin possess special interest on account of their extended practical use as fusible alloys and as bearing metals. Of the four possible ternary series, one (the Pb, Bi, Sn series) has been thoroughly investigated—as regards both constitution and physical properties—by Charpy.[1] Two others, the Sn, Cd, Pb series, and the Sn, Cd, Bi series, have been investigated from the standpoint of constitution by Stoffel.[2] The following paper deals with the constitution of the remaining ternary series: the lead-bismuth-cadmium series. My object in undertaking this investigation was to complete the fundamental data necessary for systematic work on the constitution of the quaternary alloys of the four metals.

The thermal examination and representation of this ternary series bases itself, in the first place, on an accurate knowledge of the constitution diagrams of the three binary series of alloys: those of lead-bismuth, lead-cadmium, and cadmium-bismuth. For reasons given below I have thought it necessary or advisable to re-determine the diagrams for two of these binary series.

Practical Methods and Precautions.—The metals used by me contained the following impurities:

Lead..............	0.0002 per cent. of iron.
Cadmium..........	0.004 per cent. of iron, and a trace of arsenic.
Bismuth...........	0.002 per cent. of iron, and a trace of arsenic.

In every case the weight of alloy taken for a cooling-curve observation was 40 grams. The weighed metals were melted together in a small Battersea gold-annealing crucible under paraffin (or in a stream of carbon dioxide), and the mixture was thoroughly stirred and cast in a clean brass mold. Small pieces were then cut from every portion of the solid alloy and preserved for use as seed. In a few cases the alloy to be used as seed was pipetted out of the well-stirred molten alloy.

The apparatus used for cooling-curve work consisted of a small Battersea crucible resting in an asbestos bed inside a graphite crucible, which in turn was embedded in a mixture of sand and kieselguhr contained in a sheet-iron vessel. The thicknesses of the layers of heat-insulating materials necessary to give a convenient rate of cooling were found by a few preliminary trials. The previously prepared alloy was melted (under paraffin) in the small crucible on a separate stand, the crucible was then bedded snugly in the asbestos nest, the stirrer and thermometer were warmed, and the composite crucible was then swung into position below the thermometer and stirrer, and raised until the thermometer bulb just cleared the bottom of the crucible. The outside iron vessel was then heated until the alloy was a few degrees below its first (upper) freezing point. The flame was then removed. The temperature continued to rise, until the alloy was melted and heated (usually) about 20° or 30° above its melting point. The stirrer was then started and the apparatus was allowed to cool to a convenient point for beginning the observations. With this arrangement it was not necessary to disturb anything but the small (inner) crucible, and it was found that the rate of cooling, between halting points, varied only very slightly in individual observations during the whole investigation.

---

[1] "Contribution à l'Étude des alliages," 1901, p. 200, Paris.

[2] *Z. anorg. Chem.*, 53, 137.

Both my own earlier experiences, and deductions from the published work of other investigators, have convinced me that it is a difficult matter entirely to prevent undercooling—and, moreover, that the errors caused by this lag may, under certain conditions, be very great. I therefore took special care to provide for efficient stirring, and for the systematic and periodical addition of seed. Stirring was done by means of a glass rod bent into a circle at its lower end and embracing the stem of the thermometer. The rod was moved vertically up and down, with a force capable of regulation, by means of a clock-work arrangement, the details of which I shall be glad to give to any one interested. The stirrer was adjusted so as to stop automatically as soon as the alloy arrived at a condition of decided pastiness during cooling. This left the observer with both hands free for other work.

Beginning at a temperature 5° or 6° above the expected upper freezing point of the alloy, small portions of the cold alloy were dropped into the crucible every fifteen seconds, and this seeding was continued until it was evident that stirring had ceased to be efficient. The results satisfy me that, in cases in which the first and second freezing points fell near together, undercooling (at the second halting point) was nearly always prevented; when the alloy was too pasty to be stirred at the temperature of the second or third halting point, undercooling nearly always took place.

The temperature was read every fifteen seconds by means of a reading telescope at such a distance as to enable the observer to reach round to the crucible to drop in seed. The thermometer was hung in a wide glass tube, reaching nearly to the crucible edge, so that it was possible to see every part of the mercury thread and to avoid errors due to sudden air draughts on the exposed thermometer stem. The thermometers used were standardized at the freezing points of lead (327°) and tin (232°), and were also directly compared with a thermometer (reading to 560°) tested by the Physikalisch-Technische Reichsanstalt on August

2, 1909. The correction for the exposed column was determined on each thermometer by actual observation of the mean temperature of the exposed column, under the conditions of use obtaining in a cooling-curve observation, and the addition of the correction $n(T—t)/6300$, in which n is the length of the projecting column in degrees, T the temperature to be measured, and t the mean temperature of the exposed column. These measurements were made twice for each thermometer. Up to about 220° the agreement between the two sets of corrections was very close; from 220° to 330° the mean of the two results was used as the correction.

THE BINARY SYSTEMS.

(a) **The Lead-Cadmium Series.**—The freezing point curve of the series has been determined in part by A. Kapp,[1] in part of Heycock and Neville,[2] and in part by Stoffel.[3] Stoffel's statement of Kapp's result does not agree with the published curve. I was unable to consult Kapp's thesis, and since, also, it seemed advisable to have a complete set of determinations made by one observer with identical metals and under identical conditions throughout, I have repeated the thermal investigation with the results given in Table I and Fig. 1. The position of the eutectic point was determined according to Tammann's method of thermal analysis, by measuring the duration of the freezing of the eutectic in each of the twelve alloys studied, plotting these times vertically beneath the corresponding percentage compositions, and continuing the curves free-hand to their intersection. Using the same weight of alloy and the same conditions of cooling in each case, the measured times are proportional to the amounts of eutectic present in the various alloys.

Free-hand prolongation of the upper curves points to the eutectic composition as 82.6 per cent. by weight of Pb, 17.4 per cent. by weight of Cd. This corresponds to 72.04 atomic per cent. of Pb. The prolonged time curves intersect at about 82 per cent. by weight of Pb. (I have purposely used weight percentages in constructing the diagrams, since I consider that, in spite of certain drawbacks, this method enables one to form a mental picture of the relations more easily than the use of atomic percentages. For all important points, however, I have added the atomic figures.)

The freezing point of the eutectic I have taken as 247.3°, as given by the alloys m, j, b, c, and d. The other alloys (more widely removed from the eutectic composition) were all slightly undercooled. The result agrees well with that of Kapp —249°.

On the cadmium side the freezing-time curve points to a slight solubility of lead in solid cadmium. On the lead side the limit of miscibility indicated is about 3 per cent. (by weight) of cadmium. Herschkowitsch

---

[1] Dissert., Königsberg, 1901.

[2] *J. Chem. Soc.*, 61, 888 (1892).

[3] *Z. anorg. Chem.*, 53, 137 (1907).

TABLE I.—THE LEAD–CADMIUM SERIES (BARLOW).

Alloy No.	Percentage composition.				Temp. of first halting point.	Temp. of eutectic crystallization.	Duration of eutectic freezing in 15-second units.
	Weight, per cent.		Atomic, per cent.				
	Pb.	Cd.	Pb	Cd.			
*........	100 0	0	100.0	0	327.0	...	....
a........	90.0	10.0	83 01	16 99	271.0	246.5	10.0
k.......	85.0	15 0	75.45	24.55	252.0	245.6	17.0
m.......	83.5	16.5	73 30	26.70	249.2	247.3	18.5
j........	82.0	18.0	71.18	28 82	248 4	247.3	21.0
b........	80.0	20.0	68.46	31.54	253 5	247.3	19.0
c........	70.0	30.0	55 87	44.13	265.0	247.1	15.0
d.......	60.0	40 0	44.88	55.12	272.6	247.2	11.0
e........	50.0	50 0	35 18	64.82	275.5	245.6	10.0
f........	40.0	60.0	26 56	73 44	278.4	245.6	8.5
g	30.0	70.0	18.87	81 13	281 6	246.2	6.0
h.......	20.0	80.0	11.95	88.05	290.2	246.8	4.0
i.	10.0	90 0	5.69	94 31	301.0	245.6	1.75
*	0 0	100.0	0.00	100.0	320.7	...	..

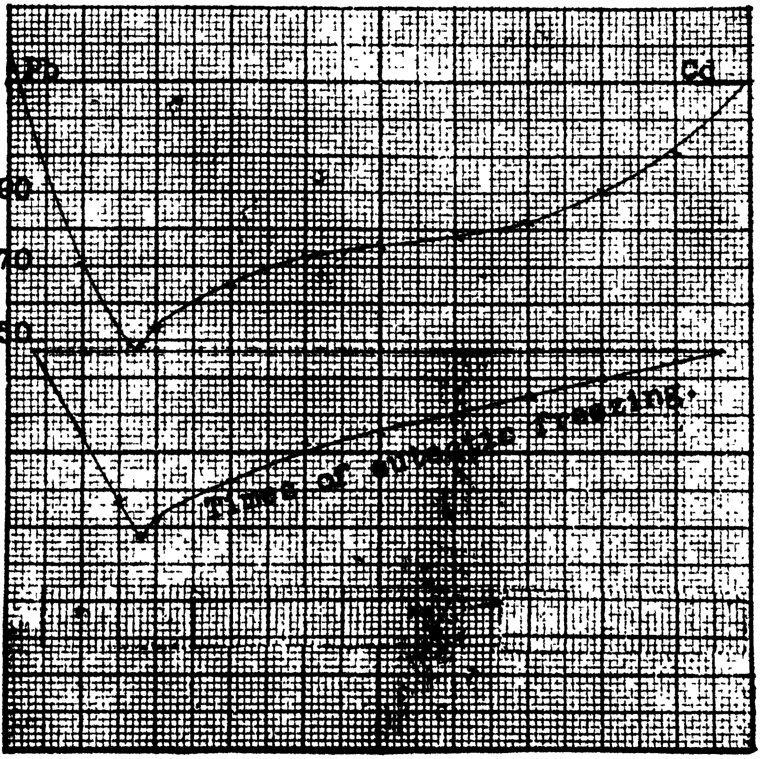


Fig. 1.—Pb–Cd series (Barlow).

(by measuring the electromotive forces of lead-cadmium alloys) found that cadmium forms mix-crystals with lead up to about 4 per cent. (atomic) of cadmium. This is 2.3 per cent. by weight. The times were measured from the cooling curves plotted on co-ordinate paper, and are given in units of fifteen seconds. The error is probably less than one time-unit in every case.

(b) **The Lead-Bismuth Series.**—The freezing-point curve has been determined by Kapp and by Charpy,[1] and is given in the upper part of Fig. 2 in weight percentages. The eutectic lies at 56.5 atomic per cent. Bi (56 6 weight per cent. Bi) and 125° C. The irregularity of the curve

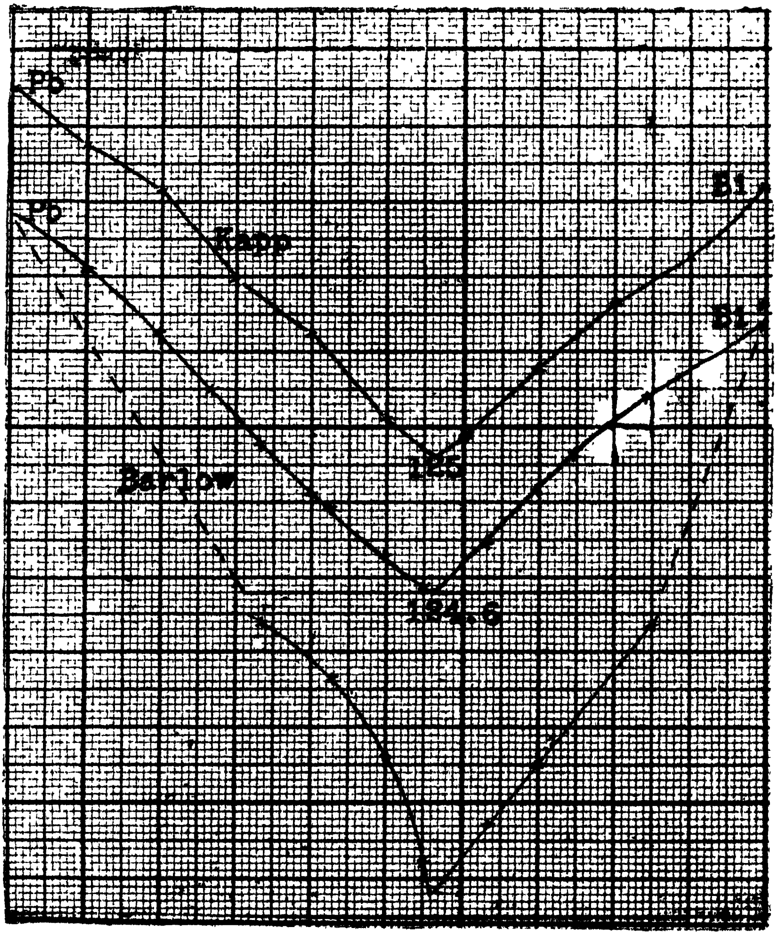


Fig. 2.—Pb-Bi series (Barlow).

---

[1] *Bull. soc. encour.*, 1901.

on the lead side led me to repeat the thermal analysis, with the results given in Table II and the lower part of Fig. 2.

TABLE II.—THE LEAD–BISMUTH SERIES (BARLOW).

Alloy No.	Composition. Weight, per cent. Bi.	Pb.	First halting point.	Second halting point.	Duration of eutectic freezing.
*	0.0	100.0	327.0	....	....
a	10.0	90.0	297.3	not seen	....
b	20.0	80.0	260.6	not seen	....
c	27.0	73.0	232.6	not seen	....
d	33.33	66.66	204.0	122 u. c.	less than 1
e	40.0	60.0	177.3	119 u. c.	not taken
f	42.85	57.15	170.6	117.2 u. c.	7.0
g	50.0	50.0	144.4	121.7	15.0
h	55.0	45.0	126.9	123.2	26.0
i	63.5	36.5	150.5	124.3	22.0
j	70.0	30.0	178.5	124.3	16.0
k	75.0	25.0	198.3	124.8	not taken
l	85.0	15.0	229.4	124.8	1.5
*	100.0	00.0	271.2	...	...

The eutectic, according to my results, both from the freezing-point determinations and from the times of eutectic freezing, lies at 56.5 weight per cent. Bi, and between 124.3 and 124.8°. With regard to the limits of miscibility in the solid state there is still room for doubt. Kapp and Wiedemann were both unable to observe a second freezing point in an alloy containing 30 per cent. by weight of Bi, and I have obtained almost the same limit on this side. Shepherd, on the other hand, as a result of electromotive force measurements, states that at ordinary temperatures mix-crystals are formed at each end of the series up to 10 per cent. on each side. On the bismuth side my results agree with this statement—indicating a solubility of bismuth in lead up to about 11 per cent. by weight of lead. The letters u. c. indicate "undercooled."

(c) **The Bismuth-Cadmium Series.**—The freezing-point curve has been determined both by Kapp (see above) and by Stoffel (see above). Their results (using weight percentages) are reproduced in Table III and Fig. 3. Kapp's observations on the bismuth side are too scanty to establish the course of the curve with certainty, and differ from those of Stoffel by as much as 20°. Since Stoffel has made three series of observations, with identical results, I have used his figures on the bismuth side of the eutectic, and those of Kapp on the other side, in constructing the ternary diagram. The eutectic lies at 44.5 atomic per cent. Bi (59.8 weight per cent.) and 146°. According to the investigations of Herschkowitsch and of Heycock and Neville the two metals form no solid solutions—are entirely non-miscible in the frozen state.

TABLE III.—THE BISMUTH-CADMIUM SERIES (KAPP, STOFFEL).

Composition. Weight, per cent.		First freezing point.	Composition. Weight, per cent.		First freezing point.
Cd.	Bi.	Kapp.	Cd.	Bi.	Stoffel.
90	10	297·5	40	60	146
80	20	279·0	35	65	158
70	30	254·5	30	70	176
60	40	225·5	25	75	191
50	50	193·0	20	80	206
40	60	149·0	10	90	236
20	80	185.0	..	..	...
10	90	230.0	..	..	...

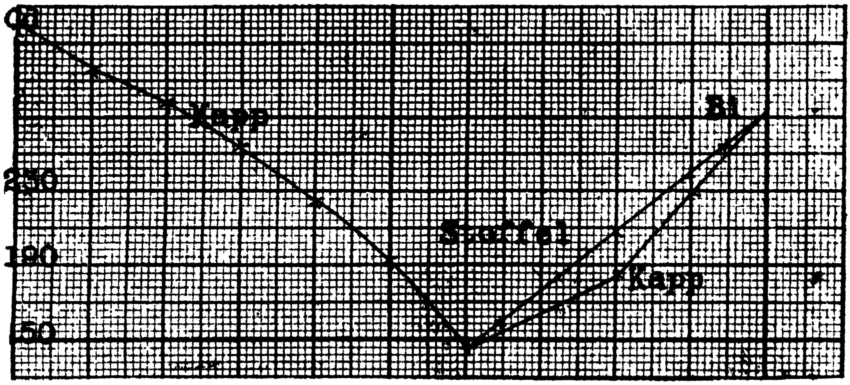


Fig. 3.—Cd–Bi series.

THE TERNARY SYSTEM: LEAD-BISMUTH-CADMIUM.

(1) **Representation of Results.**—The percentage composition of a mixture of three components may be expressed by a system of triangular co-ordinates (cutting, most simply, at 60°) in one plane. If we wish to obtain a complete representation of the equilibrium relations between the various phases of a ternary system, *temperature* must also be expressed, and must necessarily be measured along an axis lying outside of the plane of the paper, and, most simply, vertical to that plane. Within the resulting prism the seven or more surfaces of equilibrium involved may be constructed.

To represent such an equilibrium-solid clearly by a drawing is a difficult matter. If, however, we content ourselves with the representation of the upper surfaces alone (on which lie the *first* freezing points of all the possible mixtures) the projection of these surfaces on the co-ordinate triangle by means of contour lines results in a clear and intelligible diagram.

The upper surfaces of such a solid will have the general appearance of Fig. 4*a*—three more or less curved and inclined surfaces meeting in three channels or grooves (DX, EX, FX), which, in turn, dip towards their intersection at the point X. The curve ADC is the upper freezing-point curve of the binary series AC, while D represents the position of the eutectic of this series. The projection of the surfaces AEXD, etc., on the triangular plane HGK (the base of the model) would have the general appearance of Fig. 4*b*, the dotted lines representing isotherms.

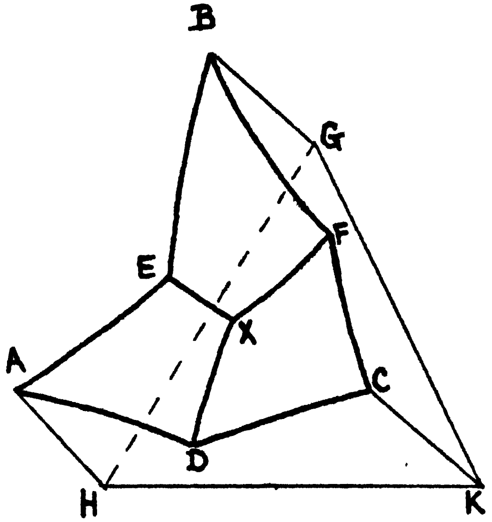


Fig. 4*a*.

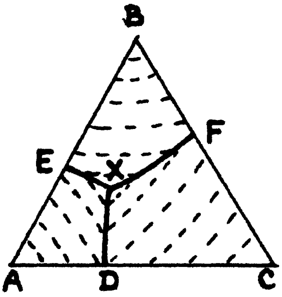


Fig. 4*b*.

Within this triangular space any point represents a mixture of the three components, A, B, C. The sum of the three lines drawn from such a point to the sides of the triangle, parallel to the sides taken in regular order, is always equal to the length of the side of the triangle. This length may be divided into 100 equal parts, when the sum of the co-ordinates drawn in this way becomes 100 per cent. of the mixture. For example, the composition marked by the point 41 in Fig. 8 is 30 per cent. Bi, 10 per cent. Pb, 60 per cent. Cd, if the measurements are made as indicated by the arrows in the margin. For a point falling on one of the sides of the triangle one co-ordinate disappears; thus the point 1 represents an alloy of composition 25 per cent. Bi, 75 per cent. Cd (the distance 1K being equal to the distance 1Bi). At the points A, B, and C, two co-ordinates vanish. A co-ordinate surface ruled according to this plan permits one to make measurements more easily than when the co-ordinates are drawn vertically to the sides of the triangle—the *altitude* of the triangle being taken as 100 per cent.

(2) Plan of Exploration.—The exploration of the upper equilibrium surfaces is best made by means of a number of *systematic* surveys, carried out and utilized as explained below. Consider, first, the freezing of the binary alloy marked 1 in Fig. 5, and assume that the two metals A and C form no solid solutions and no chemical compounds. The alloy contains more than the eutectic proportion of A. On cooling a molten mixture of this composition, freezing begins at a certain temperature. The substance which freezes out is pure A. The composition of the still molten mass therefore moves along the line AC towards C, the freezing point of the molten part gradually falling as the composition changes. When the alloy has reached the freezing point of the eutectic D the composition of the mother metal has also reached the composition of the eutectic, and the remaining melt therefore freezes completely at this temperature, before cooling farther. The solid alloy consists simply of the first-frozen crystals of pure A surrounded by the later-freezing eutectic mixture D. The cooling curve will therefore show two (and only two) sudden changes of direction (down to the point at which D has begun freezing): an upper one, at the temperature at which "excess" A begins to freeze out, and a lower one, at the temperature at which the eutectic begins (and continues) to freeze out.

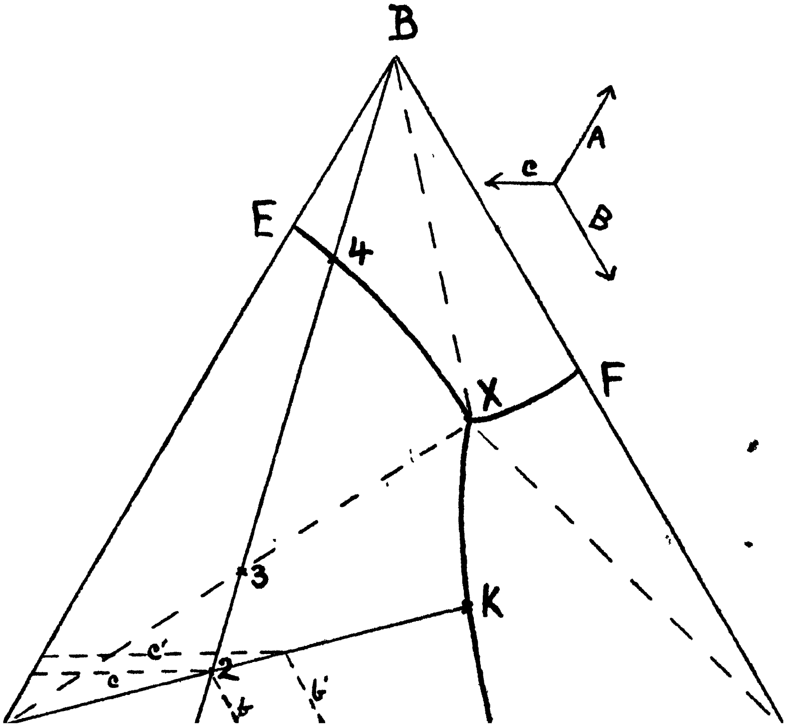


Fig. 5.

Consider, now, the freezing of the ternary alloy marked 2. At a certain temperature pure A begins to separate out. The molten part therefore becomes richer in both B and C, and both B and C are enriched in the same proportion. In order, however, that the proportion between the pairs of co-ordinates, *cb*, *c'b'*, etc., should remain fixed, the composition of the still-molten part must move along the line AK, formed by continuing the line joining A and 2. When this composition has reached the point K, all the A in excess of the binary eutectic proportion has been frozen out at a gradually falling temperature and the binary eutectic (D) begins to crystallize. The molten part therefore becomes progressively richer in B, since both A and C are being continuously removed. Solidification continues, at temperatures gradually falling, and on KX, until the temperature and composition corresponding to X are reached, when the remaining melt freezes as the ternary eutectic at a constant temperature. The cooling curve will accordingly show three sudden changes of direction down to the point at which X has begun freezing: the first at the excess A freezing point, the second at the temperature at which the binary eutectic begins to freeze, and the third at the ternary eutectic freezing point.

Suppose, now, that we observe the cooling curves of a *series* of alloys lying on the line 1B. The first freezing points will lie on a curve sloping from both sides towards the point 4, at which the eutectic line EX is cut. The second freezing points of all alloys between 1 and 3 will fall at temperatures gradually lower and lower along the curve DX. The alloy 3 will show only two freezing points—that of excess A and that of the ternary eutectic. (An alloy whose composition falls on such a line as DX will also show only two freezing points—those of the binary and ternary eutectics.) From 3 to 4 the second freezing points will lie at points along X4, at gradually rising temperatures moving towards 4. Beyond point 4 the excess metal is no longer A, but B. Alloys between 4 and B begin separating pure B at certain temperatures, the composition of the molten part moving towards the line EX, and cutting it in every case at the point 4, and then following the curve 4X. In other words, the second freezing point of all alloys between 4 and B is fixed at the temperature indicated by 4.

If we consider the alloy 1 as a single component, and pure B as the second component, we can plot the first and second freezing points of the series just as in the case of a system of two elementary components, and we shall obtain a diagram of the general appearance of Fig. 6. The temperature X is indicated (although only approximately—because of the difficulty of observing all the second freezing points with great accuracy) by the intersection of the sloping branches of the second freezing-point curves: the temperature 4 is at the intersection of the upper freezing-point curves and also at the intersection of the horizontal branch and one of the sloping branches of the second freezing-point curve.

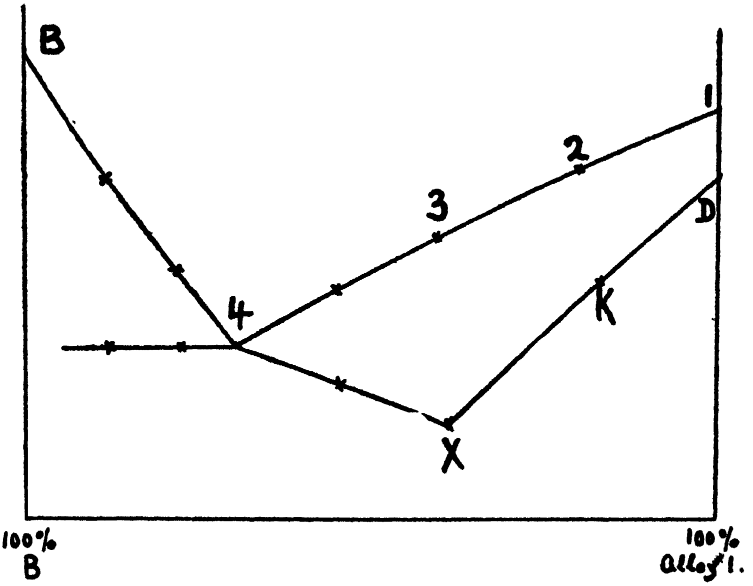


Fig. 6.

Such a survey series as 1B will furnish not only a series of first freezing points, but also an intersection on a binary eutectic line, and at least an approximation to the position of such a critical line as AX. (The line AX divides the region occupied by the alloys consisting of excess A, plus AC eutectic, plus ternary eutectic, in the solid state, from the region occupied by the alloys consisting of excess A, plus AB eutectic, plus ternary eutectic. The lines BX and CX perform analogous functions. The types included by each of the six spaces ADX, AXE, etc., will be apparent from the diagram (Fig. 5)). By taking several such surveys from each angle of the triangle we can obtain a sufficient number of binary intersections to establish the courses of the lines EX, FX and DX. The position of the ternary eutectic is established by the intersection of the binary curves prolonged, together with the approximations to the positions of AX, BX and CX, and other aids to be mentioned later.

Special Case (Survey III).—With one exception, the surveys made in this investigation are of the above type—cutting only one binary eutectic line. Survey III cuts two binary lines. The course of the two freezing-point curves may be understood by reference to Fig. 7 and the following indications:

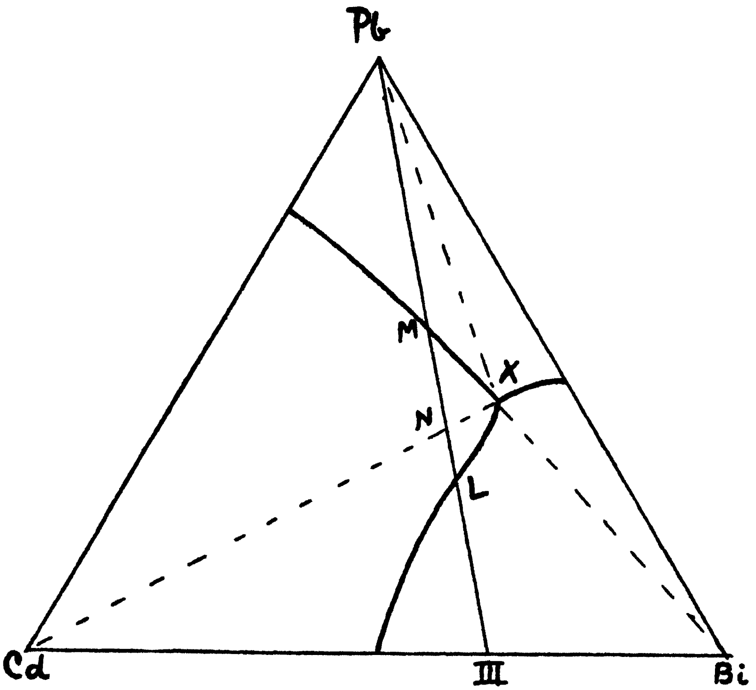


Fig. 7.

	Excess metal.	Eutectic.	1st f. p.	2nd f. p.
From III to L	Bi	Cd, Bi	falls	falls along DL
From L to N.	Cd	Cd, Bi	rises	falls along LX
From N to M.	Cd	Cd, Pb	rises	rises along XM
From M to Pb	Pb	Cd, Pb	rises	fixed at M

The actual courses of these lines are shown in Survey III, Fig. 10a.

(3) **Results.**—In Fig. 8 I have indicated the directions of the surveys used for exploration, and the compositions of the alloys actually submitted to cooling-curve observation. The alloys are numbered to aid in identifying them in the following tables and diagrams.

In Table IV, I have given the compositions, the first, second, and third freezing points of the alloys, arranged in their respective survey series. The letters n. t. signify that the halting point in question was not looked for—the observation of the cooling curve being stopped at some higher temperature. The letters u. c. indicate that the temperature was observed, but was manifestly incorrect as a result of undercooling. Pronounced undercooling was recognized at a second point only three or four times: the plotted cooling curves show that although undercooling took place in other cases, it was only very slight—not enough to interfere with the accurate determination of the freezing point, and usually extending through only a few tenths of a degree. In many cases the

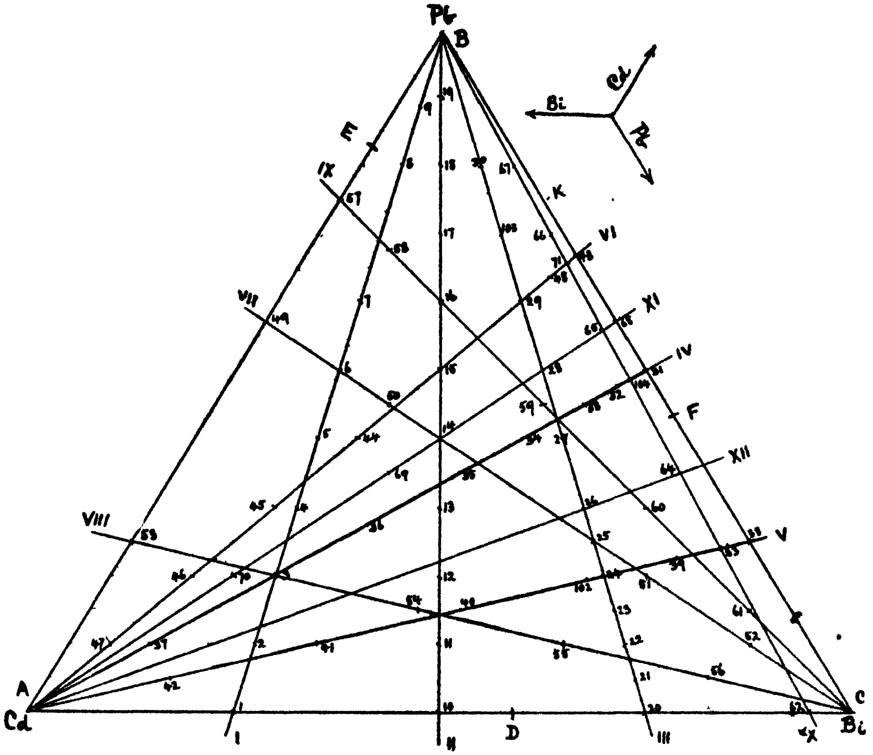

Pb
B
A
Cd
C
Bi
D
E
F
K
I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
Cd
Bi
Pb

Fig. 8.

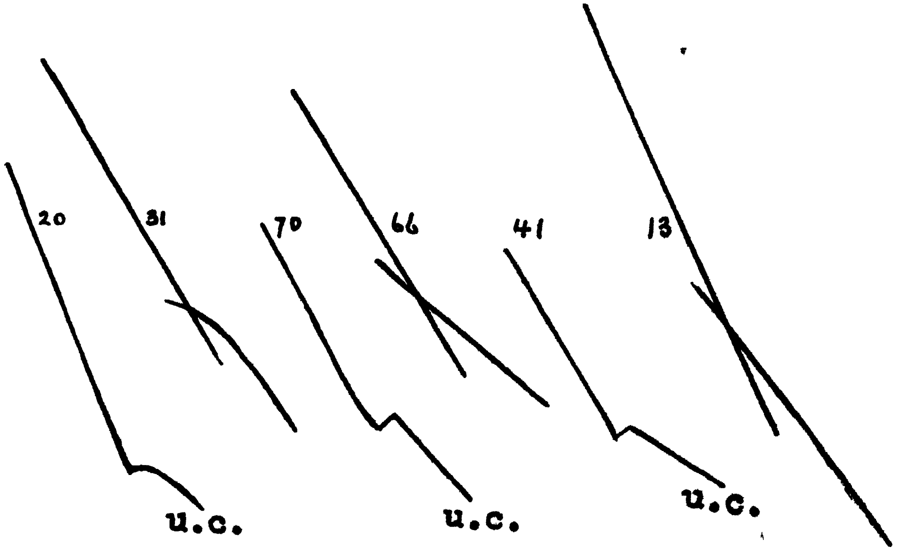

20
31
70
66
41
13
U.C.
U.C.
U.C.

Fig. 9.

two branches cut sharply. (Typical examples of observed cooling curves showing undercooling and a sharp intersection, respectively, are reproduced in Fig. 9.) Undercooling at the ternary point was naturally of more frequent occurrence, but of no importance. The ternary point was purposely not looked for in many of the alloys widely removed in composition from the ternary eutectic, since it could be determined with less likelihood of undercooling in alloys nearer the eutectic composition.

TABLE IV.—COMPOSITIONS AND FREEZING POINTS OF THE TERNARY ALLOYS OF LEAD-BISMUTH CADMIUM.

Survey. No.	Alloy No.	Composition Weight, per cent			Temp of freezing points.		
		Pb	Bi	Cd.	1st.	2nd	3rd.
I..	1	0.00	25.0	75.0	267.0	146.0	. . .
	2	10.0	22.5	67.5	263.5	115.0	91
	3	20.0	20.0	60.0	260.0	106.0	u. c.
	4	30.0	17.5	52.5	259.0	152.0	u. c.
	5	40.0	15.0	45.0	257.0	182.0	n. t.
	6	50.0	12.5	37.5	255.0	203.2	n. t.
	7	60.0	10.0	30.0	252.0	215.2	n. t.
	8	80.0	5.0	15.0	236.5	234.3	n. t
	9	88.0	3.0	9.0	268.0	234.3	n. t.
II..	10	0.0	50.0	50.0	191.0	143.9	none
	11	10.0	45.0	45.0	203.0	121.9	n. t.
	12	20.0	40.0	40.0	211.0	n. t.	n. t.
	13	30.0	35.0	35.0	218.6	95.0	n. t.
	14	40.0	30.0	30.0	223.0	127.8	n. t.
	15	50.0	25.0	25.0	225.5	165.4	n. t.
	16	60.0	20.0	20.0	224.5	192.0	n. t.
	17	70.0	15.0	15.0	216.0	213.0	n. t.
	18	80.0	10.0	10.0	241.8	216.2	n. t.
	19	90.0	5.0	5.0	290.0	n. t.	n. t.
III..	20	0.0	75.0	25.0	190.0	146.0, 145.0	none
	21	5.0	71.25	23.75	170.4, 169.7	135.8, 135.5	91.4
	22	10.0	67.5	22.5	156.7, 155.0	130.6, 130.0	92, 91
	23	15.0	63.75	21.25	134.6, 133.0	124.6, 124.6	92, 92
	24	20.0	60.0	20.0	119.9, 119.6	119.5, 119.2	92, 91
	25	25.0	56.25	18.75	127.6, 126.0	110.6, 110.3	91.2
	26	30.0	52.5	17.5	132.0, 132.0	not seen	92.0
	27	40.0	45.0	15.0	147.0, 146.0	98.7, 98.4	88 u. c.
	28	50.0	37.5	12.5	159.0, 159.0	128.0, 128.0	n. t.
	29	60.0	30.0	10.0	165.4, 163.5	165.4	n. t.
	103	70.0	22.5	7.5	210.0	n. t.	n. t.
	30	80.0	15.0	5.0	249.5	n. t.	n. t.
IV..	31	50.0	50.0	0.0	144.4	124.8	none
	32	47.5	47.5	5.0	118.6	100.0	u. c.
	33	45.0	45.0	10.0	125.0	108.0	n. t.
	34	40.0	40.0	20.0	180.2	107.0	n. t.
	35	35.0	35.0	30.0	212.0	107.0	n. t.
	36	27.5	27.5	45.0	243.8	107.0	u. c.
	3	20.0	20.0	60.0	260.0	106.0	n. t.
	37	10.0	10.0	80.0	284.0	n. t.	n. t.

TABLE IV (*Continued*).

Survey. No.	Alloy. No.	Composition. Weight, per cent.			Temp. of freezing points.		
		Pb.	Bi.	Cd.	1st.	2nd.	3rd.
V..	38	25.0	75.0	0.0	198.3	124.8	none
	63	24.1	72.3	3.8	180.0	97.0	n. t.
	39	22.5	67.5	10.0	154.0, 156.0	108.5, 108.0	91.6
	24	20.0	60.0	20.0	119.5	119.5	91.6
	102	19.5	58.5	22.0	125.1, 124.8	118.7, 118.6	n. t.
	40	15.0	45.0	40.0	200.0	114 u. c.	92.0
	41	10.0	30.0	60.0	246.6, 248.0	u. c.	91.4
	42	5.0	15.0	80.0	282.0	u. c.	n. t.
VI..	43	66.66	33.33	0.0	204.0	124.8	none
	48	63.33	31.66	5.0	181.9	n. t.	n. t.
	29	60.0	30.0	10.0	165.4	165.4	n. t.
	15	50.0	25.0	25.0	225.5	165.4	n. t.
	44	40.0	20.0	40.0	247.5	n. t.	n. t.
	45	30.0	15.0	55.0	264.0	165.3	n. t.
	46	20.0	10.0	70.0	274.2	165.3	n. t.
	47	10.0	5.0	85.0	292.0	165.4	n. t.
VII..	49	57.14	0.0	42.86	272.0	247.3	none
	6	50.0	12.5	37.5	255.0	203.2	n. t.
	50	44.6	22.0	33.4	239.8	167 0	n. t.
	14	40.0	30.0	30.0	223.0	127.8	n. t.
	25	25 0	56.25	18.75	127.6	110.6	91.7
	51	20.0	65.0	15.0	138.0, 138.8	117.7, 117.6	92.0
	52	10.0	82.5	7.5	210.0, 212.0	118.2, 118.0	n. t.
VIII..	53	25.0	0.0	75.0	286.0	247.3	none
	3	20.0	20.0	60.0	260 0	106.0	u. c.
	54	15.0.	40.0	45.0	218.4	116.0	n. t.
	55	10.0	60.0	30.0	138 0	133.6	91.5
	56	5.0	80.0	15.0	199.0	133.6	n. t.
IX..	57	75.0	0.0	25.0	260.0	247 3	none
	58	67.5	10.0	22 5	241.8	219 6	n. t.
	16	60.0	20.0	20 0	224.5	192.0	n. t.
	59	45.0	40.0	15.0	166.0	118.5	91.5
	60	30.0	60.0	10.0	122.0	102.0	91.0
	61	15.0	80.0	5.0	208.6	102.4	92.0
X..	62	0.0	95.0	5.0	253.0	146 0	....
	63	24.1	72.3	3.8	180.0	97.0	91.0
	64	35.0	61.75	3.25	139.0	103.0	91.0
	104	48.7	48.7	2.6	130.0	108.7	91.0
	65	56.0	41.8	2.2	156.0	109.0	u. c.
	71	65.5	32.7	1.8	194.0	109.0	n. t.
	66	70.0	28.5	1.5	218.0	n. t.	n. t.
	67	80.0	19.0	1.0	254.0	n. t.	n. t.
XI..	68	57.15	42.85	0.0	170.6	124.8	none
	65	56.0	41.8	2.2	156.0	109.0	n. t.
	28	50.0	37.5	12.5	159.0	128.0	n. t.
	14	40.0	30.0	30.0	223.0	127.8	n. t.
	69	35.0	26.25	38.75	240.0	132.0	n. t.
	70	20 0	15.0	65.0	269.6	131.0	n. t.

In Figs. 10*a*, 10*b*, 10*c*, I have represented the sections revealed by the survey lines, and also the second freezing-point curves. It should be

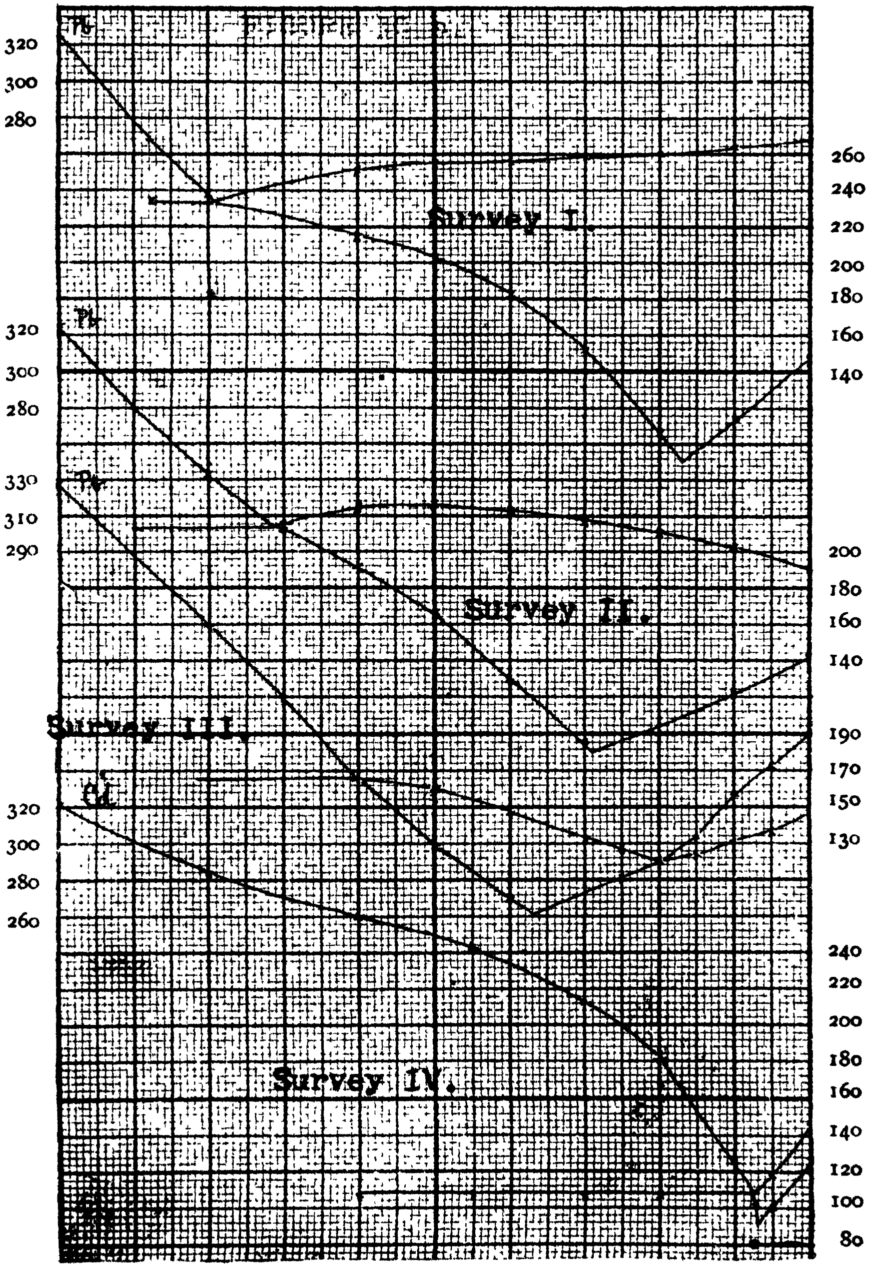


Fig. 10*a*.

understood that the *compositions* corresponding to the observed *second* points (with one exception) are not known at the time of making the survey. They lie, of course, somewhere on the respective binary eutectic lines, but the exact courses of these lines are not known at this stage

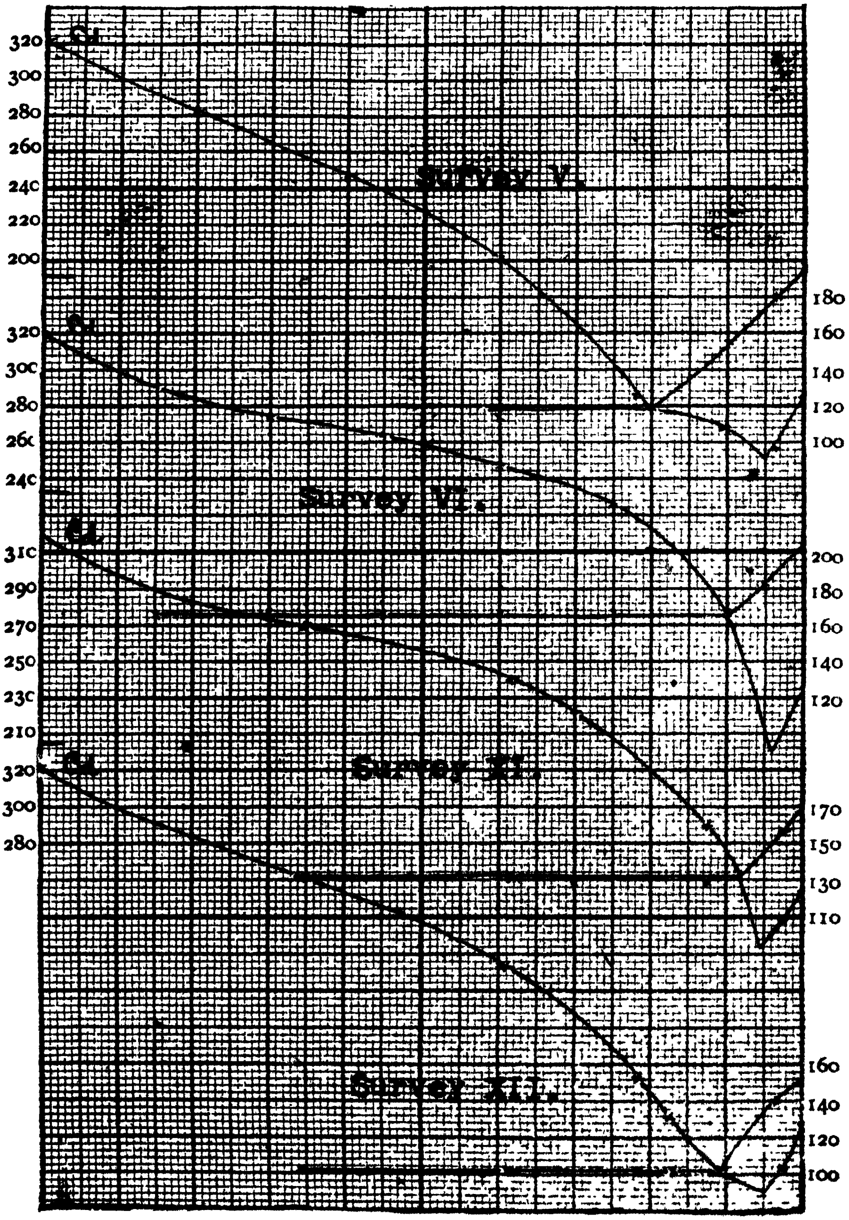


Fig 10b.

of the investigation. The one point in each survey which can be directly utilized is that at which the survey line cuts the binary eutectic line; both the temperature and composition represented by this point can be determined with considerable accuracy. I have shown below how the other observed second points in a survey series may be made use of to

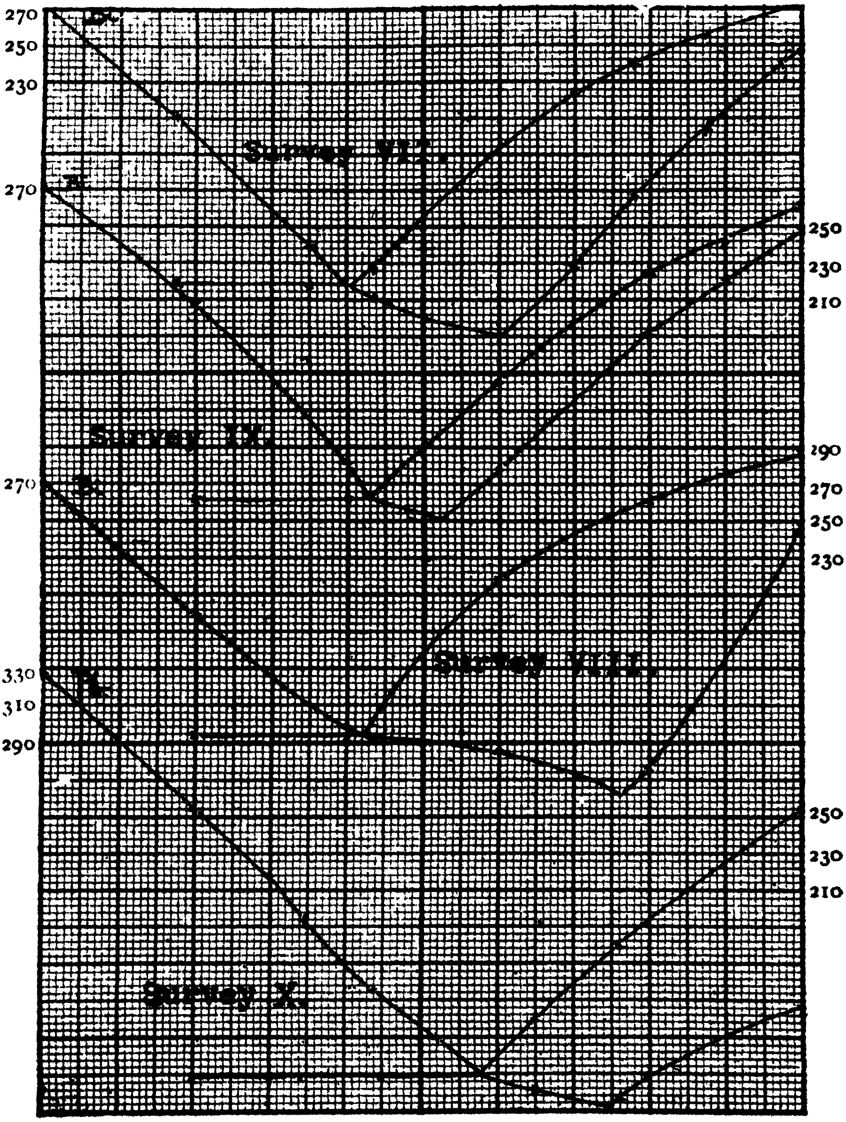


Fig. 10c.

check the courses of the eutectic lines after these lines have been determined from the survey-eutectic line intersections.

Many of the cooling-curve observations were repeated. In some cases both results are given in Table IV, in order to show the sort of agreement obtained. In other cases the average of the two (or three) results, or the single result, is used.

(4) **Construction of the Ternary Diagram.**—The first step was to mark on the triangular co-ordinate surface the positions of the survey lines, and the first freezing points observed at the respective compositions. The next step was to mark on the sides of the triangle points showing the positions of the three binary eutectics, and also a series of first freezing points (on each side of the triangle) ten degrees apart—taking these points from the binary diagrams shown in Figs. 1, 2, and 3.

The next step was to establish the direction of each one of the binary eutectic curves. For this purpose the intersections of these curves by the eleven survey lines were used. These intersections are given in the subjoined table (Table V):

TABLE V. SURVEY-BINARY CURVE INTERSECTIONS.

Survey No.	Composition at cut. Weight, per cent			1st and 2nd freezing points.
	Pb.	Bi.	Cd.	
I	78.5	5.375	16.125	234.3
II	71.2	14.40	14.40	214.0
III*a*	20.0	60.0	20.0	119.5
III*b*	60.0	30.0	10.0	165.4
IV	46.0	46.0	8.0	108.0
V	20.0	60.0	20.0	119.5
VI	60.0	30.0	10.0	165.4
VII	23.09	59.6	17.31	118.0
VIII	10.5	58.0	31.5	133.6
IX	32.25	57.0	10.75	102.0
X	42.7	54.435	2.865	109.0
XI	52.57	39.43	8.0	131.0

The cut on Survey V is actually at 20.5 per cent. Cd, and about 119°, while the cut on III is at 20 per cent. Cd. These points lie so near together that they are taken as coincident in the ternary diagram at alloy 24—the temperature assigned being 119.5°. Through the intersections found above, the curves DX, EX, and FX were drawn, as far as the points on IX, IV, and X, respectively. As an aid to the free-hand prolongation of these curves, and as a means of checking the accuracy of the work done, four additional check (or secondary) surveys were made: Survey XII, from Cd to Pb, 36.5 per cent.; Bi, 36.5 per cent. Survey XIII, from Cd to Pb, 40 per cent.; Bi, 60 per cent. Survey XIV, from Cd to Pb, 46.5 per cent.; Bi, 33.5 per cent. Survey XV, from Bi to Cd, 9.7 per cent.; Pb, 90.3 per cent. Survey XII, included in Fig. 10*b*, may serve as an example of the results obtained by these secondary surveys. The following observations were used in constructing the curve:

	Pb.	Bi.	Cd	1st point.	2nd point.
Cut on I.	12.5	21.87	65.63	262.0	103.0
Cut on VIII.	17.5	30.0	52.5	241.0	96.0
Cut on II.	22.0	39.0	39.0	213.0	102.0
Cut on VII	28.57	50.0	21.43	153.0	102.0
Cut on III	30.0	52.5	17.5	132.0	102.0
Cut on IX	32.62	56.5	10.87	101.8	101.8
Cut on X . .	35.0	61.75	3.25	139.0	103.0
Cut on Pb–Bi	36.5	63.5	0.0	150.0	124.8

The temperatures assigned are taken from the previously completed curves for Surveys I, VIII, etc.

The other secondary surveys (XIII to XV) give curves almost as smooth as XII. To avoid crowding the diagram, and because no *new* experimental results are involved, Surveys XIII to XV are not inserted in the main diagram. Their cuts on the curves DX, etc., were, however, used provisionally as guides in prolonging these curves.

The next step in the construction of the ternary diagram was to establish temperatures differing by 10° on the eutectic curves. For this purpose I fitted the edge of a strip of co-ordinate paper to the curve as drawn, and marked on the paper the intersections of the survey lines with the binary lines. I then removed the paper strip, erected perpendiculars at the points marked, proportional to the temperatures indicated, completed the curve free-hand, made marks at the edge of the strip vertically beneath temperatures differing by 10°, and finally replaced the strip and transferred the marks to the binary eutectic curves.

Before using the points so found as starting points from which to begin drawing the isotherms, I checked their positions as follows: The second freezing point of alloy No. 2 was observed at 115°. A straightedge placed so as to join Cd with alloy No. 2 cut the curve DX at, or

Alloy.	Observed. 2nd point.	Binary cut (See above)	Alloy.	Observed 2nd point.	Binary cut (See above.)
2	115.0	about 116.0	17	213.0	213.0
3	106.0	about 108.0	21	135.8	about 137.0
4	152.0	about 153.0	22	130.6	about 130.6
5	182.0	about 184.0	23	124.6	about 125.0
6	203.2	about 205.0	24	120.0	about 120.0
7	215.2	about 217.0	25	110.7	about 112.0
11	121.9	about 130.0	27	98.7	about 97.0
13	95.0	in the gap	28	128.0	about 130.0
14	127.8	about 130.0	39	108.0	about 108.0
15	165.4	about 165.4	50	167.0	about 170.0
16	192.0	about 192.0	54	116.0	about 117.0
			58	219.6	about 222.0
			59	118.5	about 117.0
			63	97.0	in the gap

about, 116°. This agreement confirms the positions of the points assigned to 110° and 120° on curve DX. Proceeding in this way I obtained the following checks. Except for alloy No. 50 (and possibly alloy No. 58) the results justified me in using the points marked on the binary curves.

The isotherms were then drawn in, and Fig. 11 was produced. For the sake of attaining clearness in reproducing the diagram on a small scale I have marked only the positions of the isotherms, the binary eutectic curves, and the ternary eutectic. The investigated alloys are shown in Fig. 8. The data for these alloys can easily be found by reference to Table IV.

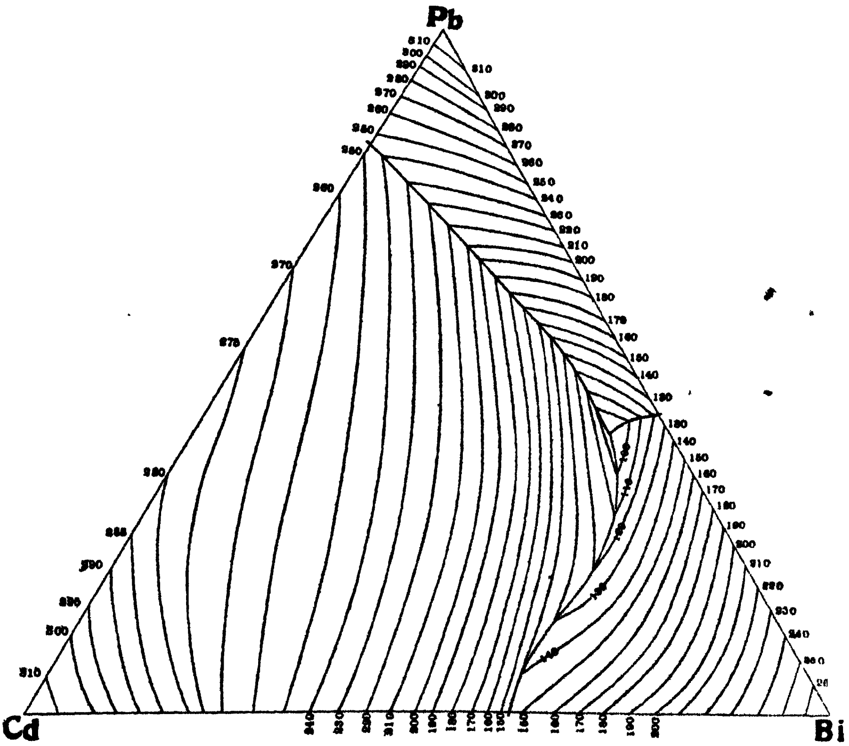


Fig. 11.—Isotherms of first freezing-points of cadmium-bismuth-lead alloys (Barlow).

REMARKS ON THE TERNARY DIAGRAM.

The three-curved surfaces all present convex sides towards the angles of the triangle. In other words, the depression of the freezing point of bismuth (for example) caused by the addition of a small amount of either lead or cadmium alone is less than that produced by the addition of an equal weight of a *mixture* of lead and cadmium; so, too, for the depression of the freezing point of lead and of cadmium.

The gradual and peculiar alteration (near the cadmium angle) of the course of the isotherms running from EX to the Cd–Bi line is what might have been expected from the shape of the freezing-point curve of the lead–cadmium series—and to some extent also from that of the lead–bismuth series. (In order to follow this gradual change of course I have inserted three isotherms between the ten-degree steps near the Cd angle.) Thus the Cd–Pb freezing-point curve shows an *inversion* from concave (from above) to convex at about 50 per cent. Cd, or about where the 275° isotherm emerges on the Pb–Cd side of the ternary diagram. In accordance with this the ternary isotherms are concave between Cd and, say, the 280° isotherm, almost straight from this point to the end of Survey VII, and gradually become convex from VII on to the eutectic E. On the Cd–Bi side the ternary isotherms retain their concavity up to the 250° isotherm—which is almost a straight line for the greater part of its course. In both cases the inversion in the freezing-point curve of the binary series evidences itself in the ternary diagram. From 250° on, towards the ternary eutectic, the isotherms are very nearly parallel.

The Ternary Eutectic.—The curves DX, EX, FX, continued free-hand from their cuts on IX (and XII), IV, and X (and XV), respectively, intersect at about 8 per cent. Cd, 40 per cent. Pb and 52 per cent. Bi.

An alloy of 5 per cent. Cd, 40 per cent. Pb, 55 per cent. Bi, was allowed to cool to 91.5°, with constant stirring and seeding, and a part of the still molten substance was then drawn by means of a suction pump into a glass tube provided with an asbestos filtering plug at its lower end. This, on analysis, gave Pb 41.1 per cent., Bi 50.5 per cent., Cd (by difference) 8.4 per cent. I am not convinced, however, of the possibility of so regulating the tightness of the asbestos plug and the force of the suction as to prevent minute crystals of a frozen excess metal, or a frozen binary eutectic, from being mechanically washed up into the tube with the molten ternary eutectic.

Cooling curves were taken of a number of alloys near the composition just given. Two of these alloys showed a very slight pause at 92°, and a sharply defined ternary freezing point at 91.4 to 91.5°. The composition of the ternary lies very near this point and may be taken, for the present, as Pb 40.2 per cent., Bi 51.65 per cent., Cd 8.15 per cent. The freezing point, as a mean of twenty determinations, lies at 91.5°, and this number, in fact, was found in the four or five cases in which special care was taken to observe the point accurately. It is interesting to note that, of the four possible *ternary* eutectics of the four metals (Sn, Cd, Pb and Bi), this one has the lowest freezing point. The ascertained temperatures are:

Sn–Cd–Pb,	Stoffel,	145°
Sn–Cd–Bi,	Stoffel,	103°
Sn–Pb–Bi,	Charpy,	96°
Pb–Bi–Cd,	Barlow,	91.5°

NOTE.—In sixteen of the alloys investigated a transformation point was noted (in addition to the three freezing points) at a fixed temperature, approximately 124°. In every instance observed the transformation took place below the temperature at which binary eutectic had begun freezing. The phenomenon was not noticed early in the investigation, and the data at hand are not sufficient to enable me to fix the limits of composition within which the change takes place. If the halt is caused by the formation in the partly-solid alloy of a binary or ternary compound, the extent to which this compound may form mix-crystals with the three pure metals will decide whether it is necessary to introduce another surface—roughly triangular in outline—at the point now assigned to the ternary eutectic. I intend to resume the investigation of the transformation at an early date, and ask for a reasonable time reservation for this purpose.

METALLURGICAL LABORATORY, VIRGINIA POLYTECHNIC INSTITUTE,
BLACKSBURG, VA.

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

STUDIES IN VAPOR PRESSURE: III. A STATIC METHOD FOR DETERMINING THE VAPOR PRESSURES OF SOLIDS AND LIQUIDS.[1]

BY ALEXANDER SMITH AND ALAN W C. MENZIES.

Received August 20, 1910.

This paper consists of five sections dealing, respectively, with:

(1) The sources of error of a more general character involved in vapor pressure measurement.

(2) A critical résumé of the characteristics of the older methods, with particular reference to the individual sources of error in each.

(3) A description of the present apparatus.

(4) A criticism of this apparatus, in relation to the various sources of error.

(5) A set of measurements of the vapor pressures of water, made with a view to testing the efficiency of the apparatus.

The apparatus was applied in a redetermination of the vapor pressure of mercury, and in a quantitative study of the chemical constitution of calomel vapor, which will be described in separate papers.

Section 1. General Sources of Error Involved in Vapor Pressure Measurement.

A critical study of the very voluminous literature of vapor pressures reveals the fact that, where two or more independent series of values for the same substance are in existence, inconsistency is the rule and substantial quantitative agreement throughout two comparable series the exception. The differences range from a few tenths of a millimeter to several hundred millimeters.[1] In view of this discordance, which affects also our own results when they are compared with those of others, some space must be taken to discuss the general sources of error in the measurement of vapor pressure and to give some account of the older methods. The aim of this discussion is to attempt to indicate the precise conditions that must be met if these chief sources of error are to be avoided. When the sources of error have thus been defined, it is possible to show how far the method described in this paper meets the required conditions, and how far confidence may be placed in the experimental results secured by its means.

---

[1] This paper, and the two following, were read at the Boston meeting of the Society, on Dec. 30, 1909.

The sources of errors that are common to most methods of vapor pressure determination may, perhaps, be best discussed under the three heads of temperature, pressure, and impurity of material:

Temperature.—(*1*) *Steadiness and Equal Distribution.*—When the condensing vapor from a liquid boiling in a flask is used to maintain a steady temperature, the vapor, at first inevitably superheated, is expected to cool itself to the boiling point by radiation and by giving up heat to the bodies that it encounters. If the latter are too thoroughly jacketed, they may not lose the heat sufficiently fast to cool to the boiling point the vapor in the neighborhood of the thermometer. Errors, therefore, arise when the boiling is rapid, or when a sand bath or other large radiating surface is used as a source of heat. With inadequate jacketing, on the other hand, the latent heat of the vapor may be insufficient to raise the temperature of the heated bodies to the boiling point. This is a common experience, for example, in determining the sulphur boiling point of a platinum thermometer. In this connection it has not always been borne in mind that the latent heat of evaporation of water is exceptionally high, that of other liquids having, at their boiling points, only a fraction of the value for water. Again, when the liquid is boiled under reduced pressure,[2] the mass of vapor condensing is necessarily smaller, and its heating power, in virtue of latent heat, much less. It will be seen that, for a steam jacket, a much greater latitude in strength of heating (*e. g.*, of flame-height) is possible than for other jacketing vapors.

Liquid baths, having a large volume and therefore a large heat capacity, have generally been found satisfactory in maintaining steady temperatures whenever the stirring was adequate (see Section 3, below), which, however, has not always been the case. Air baths, on account of their small heat capacity, are far inferior,[3] and when employed have frequently not been stirred at all.

---

[1] See Landolt and Börnstein's, or any similar set of tables.

[2] As in Ramsay and Young's method of securing any desired temperature from 0° to 360°, by use of eight liquids (*J. Chem. Soc.*, 47, 640; 55, 483).

[3] See, *e. g.*, this series, No. V, following.

(*2*) *Accurate Determination of Actual Temperature.*—Explicit statements of the method of standardization of the thermometers used and of the degree of probable accuracy in the measurement of temperature are frequently wanting. In mercurial thermometry, it may be mentioned, the correction for external pressure upon the bulb is very uniformly omitted (see Section 2, below); too much faith is placed in an arithmetical correction for "exposed thread;" and readings to tenths above 300° are treated with too much respect.

(*3*) *Scale of Temperature.*—In few cases is the scale specified or, apparently, considered. Since even so low as 200° the difference between the constant-pressure air scale and the thermodynamic scale is of the order of 0.1° (corresponding to a pressure difference of several mm.), and at 450° the difference is nearly 0.5°, it would appear that many refinements in measuring or calculating pressures to single millimeters, not to speak of tenths, hundredths, and even thousandths of a mm. that are found in the literature, are really superfluous.

As a sample of vapor pressure thermometry, similar to dozens that might be cited, the determination of the vapor pressures of iodine by E. Wiedemann[1] may be mentioned. At 180°, for example, he found the value 687.2 mm. Since he says nothing about the style of the thermometer, about corrections, or about the scale of temperature referred to, two of these figures in the pressure are without significance. It is not remarkable, therefore, that the value is 25 mm. (corresponding to nearly 1.5°) divergent from that of Ramsay and Young,[2] and that his results add absolutely nothing to our previous knowledge.

Pressure.—The straightforward reduction of gage and barometer readings to mm. of mercury at 0° is not always stated to have been performed. Correction is made for the varying value of the gravity constant (*g*) only in very exceptional cases. Yet, in Chicago, a place not very elevated, and not far from 45° N. L., this correction amounts to 0.25 mm. per 760 mm., and in laboratories in London the value is about 0.5 mm. per atmosphere. This correction, therefore, usually considerably exceeds the error involved in the mere reading of the gage.

Impurity.—In the matter of purifying the crude material for the purposes of vapor pressure measurement, the physicist is usually admittedly at a disadvantage. But here even the chemist may be found somewhat unintelligently distilling "nine times" or freezing out or recrystallizing "fifteen times", with no guarantee that any increase of purity is being attained. How real is the necessity for purification may be judged from the statement of Tammann[3] that 0.01 per cent. of alcohol in benzene raised the vapor pressure of the latter, near the boiling point, by 12 mm.

---

[1] *Ber. physik. Ges.*, 3, 159 (1905).

[2] *J. Chem. Soc.*, 49, 453 (1886).

[3] *Ann. Physik*, [3] 32, 683 (1887).

A somewhat different class of impurity is met with in the moisture, oxygen, nitrogen and carbon dioxide dissolved in liquids or adhering to solid substances. Such impurities form undoubtedly a most constant and elusive source of error. The seriousness of the error due to this cause, however, varies much with the particular method employed. Attention may, perhaps, here be called to a fact which seems to be very generally overlooked, namely, that gases are, as a rule, much more soluble in other liquids than in water, and therefore, in general, have in other liquids more effective vapor pressure, and are less quickly and easily removed by boiling and other precautions than in the case of water. In the following table[1] the solubilities of three common gases are stated as volumes of gas held in solution by one volume of various liquids under ordinary conditions.

Liquid.	Carbon dioxide, 25°.	Nitrogen, 25°.	Oxygen, 20°.
Water	0.83	0.016	0.028
Carbon disulphide	0.87	0.059	...
Benzene	2.43	0.116	
Chloroform	3.43	0.135	..
Methyl alcohol	3.84	0.142	...
Acetic acid	4.68	0.119	...
Amyl acetate	4.12	0.173	..
Acetone	6.29	0.146	...
Alcohol	.	...	0.284
Petroleum	1.17 (20°)	0.117 (20°)	0.202

It may be pointed out in this connection that there is, probably partly for this reason, far less inconsistency in vapor pressure measurements of different observers in the case of water than in that of any other liquid. In many vapor pressure determinations there is no record of even an attempt to remove gases by preliminary boiling. Other observers boil for "two minutes" or for "some time." Not one of the widely used static methods admits of repetition of the boiling-out process till constant results are obtained, and thus the only sure proof of the effectiveness of the attempt to remove impurities is lacking[2] (see Section 2).

Section 2. The Older Methods.

Only certain methods will be here considered which are applicable over wide ranges of temperature, no mention being made of the tensimetric, gas-current, dew-point, and other methods of limited range. Regnault's classification of methods into "static" and "dynamic" may be followed.

---

[1] These figures are mainly from Just, *Z. physik. Chem.*, **37**, 354.

[2] A re-opening of the apparatus and repetition of the boiling out, or some equivalent process, so far as we have noticed, is mentioned only as follows: Ramsay and Young, *Phil. Trans.*, **177**, 91 (1888), part of the observations with a single substance (NH_4Cl) only. Lescoeur, *Ann. chim. phys.*, [6] **16**, 389 (1889). Beckmann, *Z. physik. Chem.*, **4**, 534; Raoult, *Ann. chim. phys.*, [6] **20**, 301 (1890), liquid boiled, but not the mercury; method not applicable above 1 atm. Vanstone, *J. Chem. Soc.*, **97**, 429 (1910).

Static Methods.—As representing a large class of static methods, may be taken that form in which the substance is introduced into the Torricellian vacuum of a jacketed barometer tube. A special temperature error incident to this method arises from the difficulty of adequately stirring a tall bath of liquid, such as those used by several of the French investigators. The difficulties when the vapor of a boiling liquid is used for heating have been discussed already. The pressure measurement is naturally uncertain in those cases, which are by far the majority, where every part of the mercury column is not held at the same temperature as the vapor chamber.

But the chief source of error in this form of the static method lies in the impurity of the substance. In the first place, mercury vapor may be present as an impurity. We find Ramsay and Young at one time applying the correction for complete saturation of the vapor chamber with mercury vapor, while, under other circumstances, Young assumes the entire absence of mercury vapor. If the correction be made, its value, at least above 280°, has hitherto been uncertain. Far more serious, however, is the uncertainty as to the inclusion with the substance of gases and moisture from the air, absorbed or dissolved in the solid or liquid, or adhering to the walls of the tube. Some observers attempt merely so to fill the tube with mercury that visible bubbles are absent. In such cases large amounts of absorbed gases must be liberated when the heating begins. Even with thorough boiling out, visible bubbles (not to speak of absorbed and invisible gases) may remain.[1] To remove gaseous impurities, the most careful workers, for example, Ramsay and Young,[2] boil, first the mercury and then the substance, in the barometer tube before inverting the latter. But even in such cases, save for the few exceptions mentioned in Section 1, a repetition of the boiling out, to test the success of the procedure, has never been attempted. What would the chemist say of a gravimetric method in which heating to constant weight played no part? The adhesion of the liquid to the top of the barometer tube, frequently cited, is, no doubt, evidence against the presence of free "air," but hardly excludes the presence of dissolved and absorbed "air." It may be questioned, also, whether obtaining almost identical pressures with varying volumes of liquid and vapor is a proof of the absence of foreign matter.[1] At all events, Ramsay and Young's method, the results of which usually were satisfactory when judged by those two criteria, happened to be tested in a different way in a single instance.[2] This tube was filled with mercury, which was thoroughly boiled in the tube as usual. Without the introduction of any substance, however, this tube was heated at 280.1°, as for a determination. When the tube had cooled, a permanent gas was found to have accumulated. Calculation showed that, while the tube was at 280.1°, this gas must have exercised a partial pressure of 2.9 mm. A second heating, if attempted, might have resulted in an increase in the amount of this gas. If a substance had been added, the amount of foreign gas could only have been still further augmented, so there is no assurance that these two tests are sensitive within ±3-5 mm. of foreign gas. Ramsay and Young's results are probably not subject to a systematic error, on account of filling, of such dimensions as this, but their exactness is due rather to the skill of the experimenters than to an inevitable accuracy inherent in the method.

---

[1] Tammann, in a piece of work on the effects of small amounts of impurities (*l. c.*), boiled out thoroughly, and remarks that after this treatment there was "usually no air-bubble" in the tube.

[2] *Phil. Trans.*, 175, 461 (1884). Young, *Stoichiometry*, 131.

The U-form apparatus, used by some investigators instead of a straight barometer tube, and applicable especially to pressures over one atmosphere, is open to very similar sources of error. Of quite another type is the static method in which pressure is measured by means of the Ladenburg spiral gage.[3] Here again, however, what is chiefly to be desired is a procedure which will permit of repetition of the boiling-out process until constant results are obtained.

If an individual observer with a constant personal equation has difficulty in duplicating results by the static method, it is not to be wondered at that different observers differ among themselves. Take, for example, the vapor pressures of acetic acid at 100°, all as measured by the static method: Landolt 408.5 mm., Ramsay and Young 417 mm., Wüllner 473 mm.; those of butyric acid at 20 3°: Landolt 7.3 mm., Ramsay and Young 0.35 mm.

Not the least of the objections to the static method is the almost unbearable laboriousness of work which attempts to be accurate. Schmidt,[4] after enumerating its difficulties, including one not noted by other observers, namely that a number of barometer tubes had to be rejected before one was found in which the pressures with small amounts of vapor were not larger than with greater amounts, adds: "The static method has so many disadvantages, when compared with the dynamic, that I can only warn [observers] not to use it."

---

[1] Young, *J. Chem. Soc.*, 55, 486 (1889). Abnormalities when the proportion of the liquid phase is *exceedingly minute* have indeed been observed (Wüllner and Grotian, *Ann. Physik*, [3] 11, 545; see also Ramsay and Young, *Phil. Trans.*, 183, 107).

[2] *Phil. Trans.*, 177, 87 (1886).

[3] *Z. physik. Chem.*, 61, 458; also *Ibid.*, 68, 129. See No. V of this series.

[4] *Z. physik. Chem.*, 8, 629.

Dynamic Methods.—A simple form of the dynamic method consists in using a thermometer immersed in the vapor rising from a liquid boiling under various known pressures. So, for example, Regnault obtained his vapor pressure curve for sulphur, and Holborn and Henning their data for water. It is plain that such a method escapes the errors due to gaseous impurity, whether adhering or dissolved, and herein lies its chief advantage over the static methods. If a reflux condenser be employed, moisture and condensable volatil impurities do not escape; while if the vapor is condensed in another vessel, the less volatil impurities become concentrated in the residual liquid. In either case, if the current of vapor streaming into the condenser be a rapid one, the pressure within the flask is commonly slightly higher than the pressure at the distant end of the condenser with which the manometer is connected. Irregular boiling may cause large errors, and is difficult to prevent. Use of a stream of air entering through a capillary vitiates the results,[1] so far as their value as vapor pressure measurements is concerned. Schmidt[2] avoids bumping by placing a pad of cotton, saturated with the liquid, in the bottom of the flask. Regnault's difficulties and results in the case of mercury will be referred to later.[3]

Ramsay and Young sought to overcome the bumping and superheating difficulties, as well as the disadvantage of the large quantity of material required, and to avoid the need of a bath which could keep the apparatus at a constant and known temperature, by means of their well-known method.[4] In this, the liquid is allowed to trickle on to cotton enveloping the thermometer bulb. This bulb is situated in a flask surrounded by a bath, the temperature of which need not be constant or definitly known, but must be at least 20° higher than that shown by the thermometer. When the pressure, which is read by means of a manometer in connection with the flask, is altered, the temperature as shown by the thermometer changes spontaneously to correspond. It will be seen that the thermometer readings are subject to the correction for the "compression coefficient," as noted by us in a former paper,[5] although this correction, amounting in certain cases to nearly 0.2°, is not mentioned in any of the published descriptions of the apparatus, or applied so far as we have seen, with a single exception, on any of the numerous occasions on which the method has been employed.

---

[1] For discussion of this, and of other sources of error, see No. II of this series, THIS JOURNAL, 32, 911.

[2] *Z. physik. Chem.*, 7, 440; 8, 628.

[3] See No. IV of this series, following.

[4] *Phil. Trans.*, 175, 37 (1884); *J. Chem. Soc.*, 47, 42; Young, *Stoichiometry*, 140 Ostwald-Luther, [2] 177.

[5] THIS JOURNAL, 32, 905. The purpose of this paper, on "A Common Thermometric Error in the Determination of Boiling Points under Reduced Pressure," seems not to have been made sufficiently clear in the paper itself. Physicists have long been familiar with the "compression coefficient," although even some of them ignore

The error due to impurity is here to be looked for from the presence of air in the cotton wool and also, more especially, dissolved in the liquid. Fresh supplies of liquid with its dissolved "air" are constantly being introduced, nullifying any possibility of permanent expulsion by boiling out. The chief advantage of the simple dynamic method is thus lost, and the chief disadvantage of the static method is re-introduced. Should the liquid have acquired a non-volatil impurity, or contain by heredity an impurity less volatil than itself, it is plain that such impurity must gradually become more and more concentrated in the cotton surrounding the thermometer bulb. The method is not applicable to pressures much greater than atmospheric, or to liquids (*e. g.*, mercury) which do not wet cotton, and is of questionable value for solids.[1]

Section 3. The Apparatus.

The special feature of the submerged-bulblet vapor pressure apparatus, already described,[2] consists in the facility with which, using only a minute amount of the substance, the expulsion of dissolved and adhering impurities may be continued until constant values for the vapor pressure are secured. This important feature is precisely the one most conspicuously required to give trustworthiness to the static method and, as we have seen, most conspicuously lacking in the standard forms of apparatus working on the static principle. Now, while the bulblet method was being reduced to suitable form, we perceived that a modification of the apparatus would convert it into a static instrument. This static apparatus retained the advantages of the important feature referred to without loss of ease of manipulation, and possessed also several additional advantages over the regular static forms of apparatus. The simple bulblet was first changed by using a wider tube, instead of the capillary, and bending the lower end of the tube upwards. The whole had thus the form of a C, and an enlargement of the open end furnished a cup into which a confining liquid could be temporarily driven during the boiling-out process. The C-formed apparatus was tied to the thermometer, just as was the simple bulblet. To allow further liberty in

it in vapor pressure work. The paper dealt with the types of thermometers commonly employed by chemists, and with the considerable dilatations occurring when large intervals of pressure are concerned. The effects cannot be ignored in vacuum distillation and in vapor pressure determinations by the cotton-jacketed-thermometer method, for example, both of which are operations much used by chemists, and not hitherto associated in their minds with the necessity of employing this correction.

[1] See No. V of this series.

[2] This Journal, 32, 907.

the choice of a confining fluid, the open limb was next lengthened so as to extend above the surface of the bath. After a series of minor changes, the form described below was finally adopted.

It is necessary to describe the apparatus and the corrections used in minute detail, as only thus can the exact conditions be understood, and only thus can the data secured retain their value if, for example, sources of error which have escaped attention should subsequently be discovered.

The Isoteniscope, Bath, and Stirrer.—The substance is placed in the spherical bulb, which is about 20 mm. in diameter (Fig. 1). The confining liquid occupies the lower half of the U-tube, which is 30–35 mm. in height. The small bulbs on each limb of the U-tube prevent the ascent of the confining liquid (by suction) into the bulb or the vertical tube. For the sake of compactness, the spherical bulb is placed behind the U-tube, and not in the same plane with it as shown (for clearness) in the figure, the purpose of the apparatus being to show when two pressures have become equal, the arrangement may be called an *isoteniscope.* The present form, to distinguish it from a different one to be described in a later paper, may be called the *static isoteniscope.* A two-liter beaker of tall shape forms the bath. The vertical tube of the isoteniscope is about 24 cm. long, so that the rubber connection is sufficiently far above the heated bath-liquid.

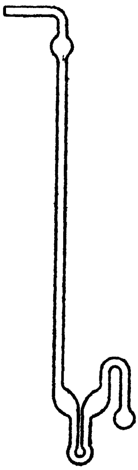


Fig. 1.

When the substance being studied is a liquid, the lower part of the U-tube is charged with *this liquid itself.* When the substance thus acts as its own confining liquid, it has the great advantage over mercury that its specific gravity is usually small. Hence, when the levels in both limbs of the U-tube appear to the eye to be identical, the error, when converted into mercury height, is negligible.

It is only when the vapor pressure of a non-fusing solid is being determined that the question of choosing a confining liquid comes up. The conditions to be fulfilled are that the confining liquid shall not have an appreciable vapor pressure of its own at the temperatures to be employed, and that the vapor of the substance shall not dissolve in it. A liquid which interacts chemically with the vapor of the substance should be avoided, especially if a gas is produced. But, as will be seen in the paper on the constitution of calomel vapor, a slow chemical action involving no gas production is not prohibitory. Among the suitable substances are mercury and melted paraffin at the lower temperatures, and fusible alloys or a molten salt or mixture of salts at high temperatures. In the case of solids, it is necessary to charge the bulb before fusing it to the U-tube.

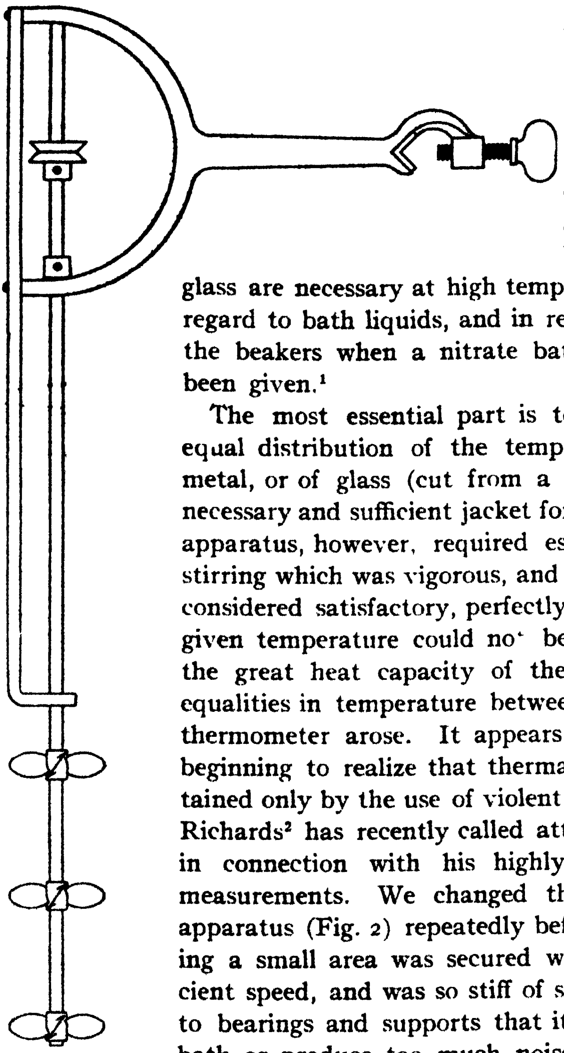


Fig. 2.

To permit sufficient immersion of the thermometer (platinum resistance, or mercury) in the bath-liquid, beakers over 23 cm. high and 11 cm. wide are used, and are filled almost to the brim. Beakers of Jena glass are necessary at high temperatures. The details in regard to bath liquids, and in regard to the handling of the beakers when a nitrate bath i, used, have already been given.[1]

The most essential part is to secure steadiness and equal distribution of the temperature. A cylinder of metal, or of glass (cut from a broken beaker), forms a necessary and sufficient jacket for the bath. The stirring apparatus, however, required especial attention. With stirring which was vigorous, and of the nature ordinarily considered satisfactory, perfectly constant pressures at a given temperature could no' be obtained. In spite of the great heat capacity of the bath-liquid, slight inequalities in temperature between the substance and the thermometer arose. It appears that chemists are only beginning to realize that thermal equilibrium can be obtained only by the use of violent, almost riotous stirring. Richards[2] has recently called attention to the same fact, in connection with his highly exact thermochemical measurements. We changed the form of our stirring apparatus (Fig. 2) repeatedly before a structure occupying a small area was secured which rotated with sufficient speed, and was so stiff of stem and so massive as to bearings and supports that it did not "whip" in the bath or produce too much noise.[3] When these conditions had been met, constant results, even with a resist-

[1] THIS JOURNAL, 32, 899.

[2] *Ibid.*, 31, 1280 (1909).

[3] The stirrer (Fig. 2) was made from an ordinary retort-stand ring. The rod (3 mm. in diameter), driven rapidly by an electric motor, rotates in two holes bored in the ring, and is supported by a stout strip of brass (seen edgewise) which extends down almost to the first vane. The length from the lower side of the ring to the lowest vane is 28 cm. The vanes are in sets of three, each set 25 mm. in diameter.

ance thermometer giving a large galvanometer deflection for one hundredth of a degree, were easily secured, where before they had seemed unattainable.

It is important to place the stirrer so that it may communicate some of its vibration to the substance (if a liquid) in the bulb. The resulting, constant agitation promotes the liberation of the vapor. It also prevents the limitation of the evaporation to the mere surface layer, a condition which would delay or prevent the complete elimination of dissolved gases.

By use of transparent quartz for the vaporizing vessel, and a quartz beaker, there is no reason why this method should not give exact determinations of vapor pressures and of dissociation pressures up to the softening point of quartz. Vapor pressures have not yet been measured accurately at such temperatures and, for dissociation pressures, the combination of a platinum heating chamber fused to a U-tube of glass, to render the confining liquid visible,[1] has several disadvantages.

The Platinum Resistance Thermometer.—While a mercury thermometer may be used, the platinum resistance thermometer is, of course, a more exact and trustworthy instrument. Quite apart from this, however, the latter has a special advantage in work of this kind, where the complete expulsion of foreign matter is ascertained by repeated observations, made at exactly the same temperature. After a second boiling out and equalization of the pressures, the temperature of the bath itself can be readjusted until the spot of light occupies its precise former position. Thus, while the actual temperature may not be known with a greater accuracy than ±0.1° or ±0.01°, according to the precautions taken, this readjustment of the bath temperature may very easily be made with an error much smaller than these.

The platinum resistance thermometer employed was of the form devised by Haagen.[2] In this form, the resistance wire is wound on a 6 cm. length of quartz tube, of diameter somewhat over 1 mm., which is then inserted into a very slightly wider quartz tube. The outer tube is then fused on to the inner one, thus embedding the resistance wire in quartz. The "bulb" so prepared is fused to a suitable length (24 cm.) of wider quartz tubing which carries the platinum and silver leads. There are no compensation leads.

For measuring resistance a Wheatstone bridge arrangement was used, with an arm ratio of 10 to 1. The box resistances, of manganin, were calibrated, and the appropriate correction applied to all measurements made. The largest error of any of the single coils employed was 2.6 parts in 10,000. The coils were not maintained at constant temperature, but, in order that the temperature correction applied might be as small as possible, the temperature of the coils was kept close to that which they possessed when the fixed points were determined. The resistance of the thermometer was about 50 ohms at 0°. The measuring current varied from 3 milli-amperes at 0° to 1.2 at 445°. No correction for heating by the measuring current was required when the thermometer was immersed in water, fused nitrates, steam at 100°, or sulphur vapor at 445°. A small correction was necessary only when moistened ice, with its badly conducting, interstitial air spaces, surrounded the thermometer bulb. The sensitiveness of the galvanometer was such that a movement of the light spot of 1 cm. on the scale corresponded to 0.04° at 0° and to 0.08° at 445°. The fixed points used were the freezing point of water, the boiling point of water and the boiling point of sulphur. The boiling point of sulphur was assumed, in accord with Holborn and Henning,[1] at 445°. Its true value may lie closer to 444.9° on the thermodynamic scale,[2] but, as this datum is liable to be changed by future observations, it was thought better to adopt the rounder number. Obtaining the ice point and the water boiling point presents little difficulty, if the usual precautions are observed. As is well known, however, the boiling point of sulphur found varies considerably with the size of the apparatus and the screening, etc., adopted.[3] We employed a gas-heated boiling tube of thin brass of 5.5 cm. diameter and 17 cm. length, jacketed by a thickness of 5-6 cm. of asbestos packing. The bulb was protected by a cone of asbestos paper, closed below, whose base was situated 10-12 cm. above the surface of the boiling sulphur and whose apex was 20 cm. below the level of condensation. We were careful to employ the roll sulphur of commerce, and used a depth of about 8 cm. Kahlbaum's crystallized sulphur contains volatile impurity. The reductions, for pressure, of the boiling points of sulphur and of water were made in accordance with the data of Holborn and Henning.[4] As the constants of the platinum thermometer are known to be changed by prolonged heating, the fixed points were redetermined whenever the thermometer had been kept long at high temperatures. The following figures will give an idea of the degree of constancy of the thermometer used, and relate to an epoch when the thermometer was being heated at temperatures of 300°-445° for many consecutive hours: 1909, October 8th, $R_0 = 50.1150$ ohms; Oct. 18th, $R_0 = 50.1161$; Oct. 22nd, $R_0 = 50.1170$. Here the total change amounts to 0.01°. The corresponding values of the fundamental coefficient were 0.00386366, 0.00386384, 0.00386671. These values approach the value for the purest platinum (0.00389).

---

[1] John Johnston, *Z. physik. Chem.*, 62, 330 (1908).

[2] *Z. angew. Chem.*, 20, 565.

---

[1] *Ann. Physik*, [3] 26, 833 (1908).

[2] See Callendar and Moss, *Proc. Roy. Soc. A*, 83, 106 (1910); Waidner and Burgess, *Bull. Bureau of Standards*, 6, 149 (Nov., 1909).

[3] See Eumorfopoulos, *Proc. Roy. Soc. A*, 81, 339 (1908); Waidner and Burgess, *Loc. cit.*

[4] *Loc. cit.*

In reducing the results, the difference formula of Callendar was employed. The constant δ changed little from 1.6147 (using 445° as the boiling point of sulphur). If a lower value is assumed for the boiling point, the value of δ is smaller. With resistance wires of impure platinum the Callendar formula requires modification.[1] To test the degree of its applicability to our wire and to ascertain whether, in the absence of compensation leads, correction was necessary for the change of resistance of the leads used, or for any other reason, two other standard temperatures were determined. Holborn and Henning[2] have determined upon their temperature scale the boiling points of naphthalene and of benzophenone, and also the changes in these boiling points for small changes of pressure. Their values are 218.039° and 306.081°, respectively; we found (a single observation) 218.075° (Δ = 0.036°), and (mean of the only two observations made) 306.089° (Δ = 0.008°), respectively. The correction to apply to the platinum temperature of our thermometer to obtain thermodynamic temperature (b. p. of sulphur 445°) is at 218°, 4.154°, while at temperatures between 0° and 100° this correction has a maximum value, at 50°, of —0.404°. Our temperature measurements may, therefore, be considered accurate to ±0.1° in the range 250°–435° and to ±0.01° in the range 50°–90°. It may be remarked that, should it seem desirable, our temperature-scale may, from the data given, be readily reduced to correspond with any other boiling point of sulphur than that here adopted.

The Pressure Gage and Barometer.—The gage consisted of a glass tube of 11 mm. inside diameter, of which the open limb and that connected with the apparatus were, respectively, 2 m. and 1.4 m. long. The latter limb was provided with a stopcock. A long mirror behind the gage eliminated the effects of parallax.

The mercury heights were measured by means of a steel tape, the gradation of which was calibrated by comparison with a standard meter. From the results of this comparison, and the coefficients of expansion of the steel and of mercury, a table of corrections covering the whole range of the room temperatures was prepared.

The mercury heights were read by means of a fine, truly horizontal hair-line ruled on a strip of glass (a microscope slide), carried by a cursor or carriage. The cursor consisted of two spring collars of brass (10 cm. apart), connected together rigidly by a metal bar which carried a horizontal arm to support the microscope slide. The brass collars grasped a

[1] Callendar, *Phil. Mag.* [5], 47, 191 (1899); Tory, *Ibid.*, 50, 421 (1900); Waidner and Burgess, *Loc. cit.*

[2] *Loc. cit.*

mandril-drawn, seamless steel tube, 18 mm. in diameter and over 2 m. in length, which was fixed in a truly vertical position. This steel tube, along with the steel tape, gage, and mirror were attached to a long board, which was suspended by a rope and balanced by a counterweight. The whole gage could thus be moved vertically between guides, in such a way as to bring to the level of the eye the point at which the mercury stood. This kept the mercury accessible to convenient observation during the numerous manipulations connected with a reading. By the use of the cursor described above the somewhat tedious use of a cathetometer was avoided, with no sacrifice of accuracy.

The heated air arising from the bath passed directly into the flues of a draught cupboard, within which the bath stood, and did not reach the gage, which was outside the cupboard. Moreover, the gage was shielded from heat radiated by the bath.

Pure mercury from the laboratory supply was redistilled *in vacuo* before use in the gage, and was tested by the method of Hulett and Minchin.[1] A portion was redistilled twice in air to oxidize the more electropositive metals, if present. The potential difference between the two samples, when placed in *N* KCl solution saturated with calomel, was less than 0.000003 volt. The metal was, therefore, of a satisfactory degree of purity.

Since an open gage was used, the barometric height had to be read. The instrument was one made by Henry Green, of Brooklyn. The scale was already corrected for capillarity. The instrument was standardized by comparison with a barometer, in which the tube was exhausted by means of a mercury pump until the McLeod gage showed a residual pressure of less than 0.003 mm. The reading of the Green barometer was found to be correct.

The following corrections were applied to the pressures:

1. The pressures were reduced to mm. of mercury at 0°. For this purpose five carefully compared thermometers, graduated to tenths of a degree, were suspended at intervals along the gage. To eliminate differences in mass and lag between the thermometers and the mercury in the gage, the bulbs of the thermometers were immersed in mercury contained in tubes of the same diameter as the gage. The coefficient of linear expansion of mercury used was 0.0001818. The error in density of mercury due to its compressibility is negligible at the pressures employed.

2. The coefficient of linear expansion of steel used in calibrating the steel tape was 0.000011.

3. The mercury heights were reduced to the sea level at 45° N. L. The value of the gravity constant, *g*, determined in the Ryerson Physical

---

[1] *Physic. Rev.*, 21, 388 (1905).

Laboratory of the University, namely 980.34, agrees precisely with that calculated from latitude and elevation. The value of g taken as the standard[1] was 980.665 cm. sec.$^{-2}$, and the factor by which the observed heights were multiplied was therefore 0.99971. The amount of this correction is thus 0.25 mm. per 760 mm.

4. In measuring the vapor pressures of water, since the temperature error in that case was less than ±0.01°, suitable correction was made for the difference in level between the cistern of the barometer and the mercury in the open limb of the gage. A similar correction was made, when necessary, for the difference in level between the surface of the water in the bulb of the isoteniscope and the surface of the mercury in the closed limb of the gage. The amount of this correction is about 0.09 mm. per meter head of air.

Other Parts of the Apparatus.—The general arrangement of the apparatus is shown in Fig. 3, which is diagrammatic. The isoteniscope and the gage were connected with a large iron bottle. Another piece of tubing leading from the bottle gave connections, by means of T-tubes, with (1) the atmosphere, (2) a vacuum reservoir and water pump, (3) a pressure reservoir, and compression pump. A stopcock on the first, and screw clamps on each of the other two tubes permitted any one to be used at will. The rubber tubing leading to the atmosphere was so long that it hung out over the edge of the base of the draft cupboard.

The water pump, with its residual pressure of about 20 mm., according to the temperature of the water, served our purpose very well, as no measurements of vapor pressures below 80 mm. were to be made. With a mercury pump, much lower vapor pressures could be studied with the same arrangement of the rest of the apparatus.

The connections were made with thick-walled rubber tubing, wired at all junctions, and coated heavily with a suitable composition. No tendency to leakage was ever observed.

The Manipulation.—The following statements apply particularly to the determinations of the vapor pressures of water below one atmosphere. The modifications required when pressures over one atmosphere are measured, or when another liquid or a solid is used, will be understood without special description.

When the temperature has reached the desired point, and has become constant, the exit to the suction bottle and pump is opened and remains open until the pressure in the iron bottle has been reduced to such a point that the water in the bulb boils, and the vapor passes freely through the confining fluid (itself also water) in the U-tube. The confining fluid is driven into the remote side of the U-tube and the bulb above it. When

---

[1] Troisième conf. gén. des poids et mésures, 1901, 66, 68.

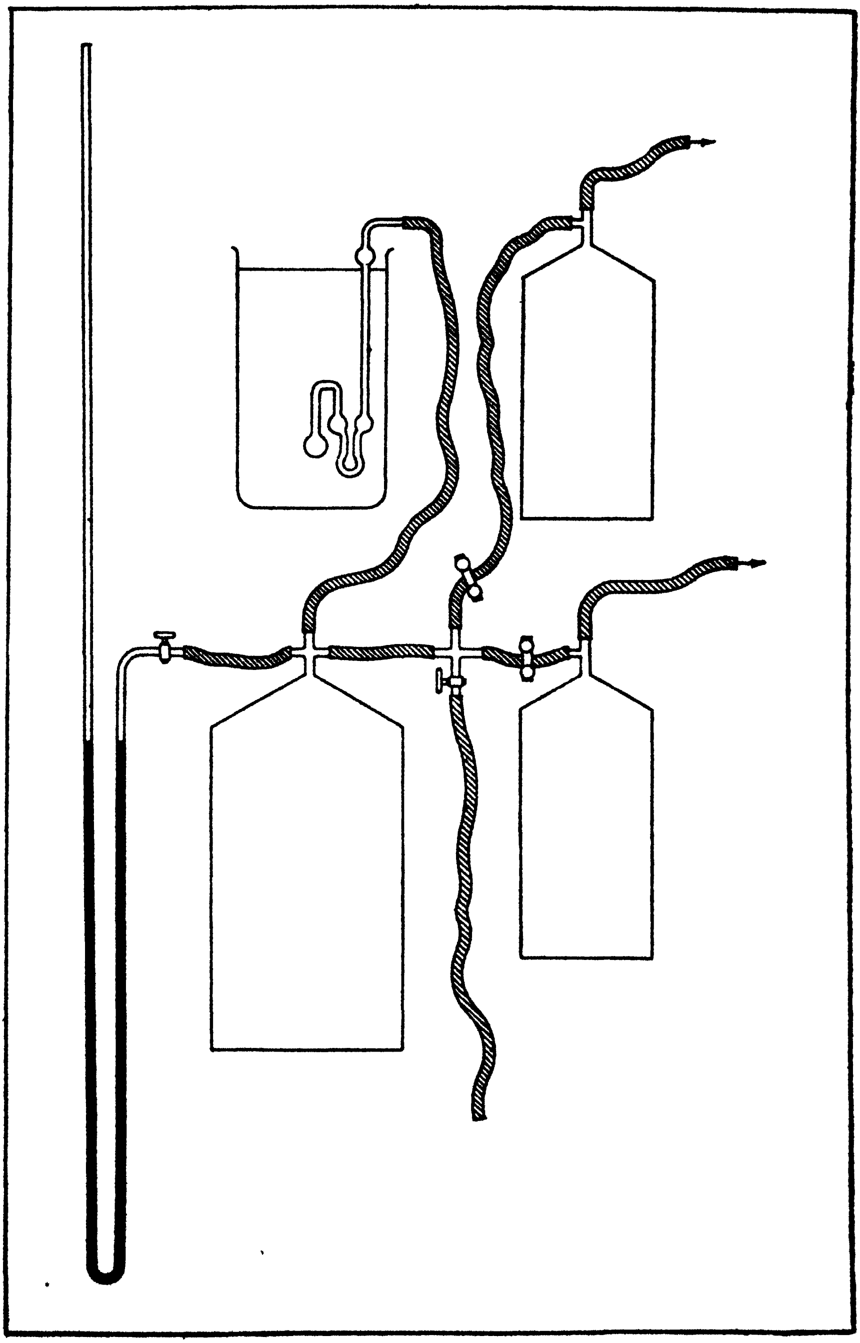


Fig. 3.

the air in the bulb, and the gases adhering to the bulb and dissolved in the water have been driven out, air is cautiously admitted to the iron bottle through the exit to the atmosphere until the levels of the water in both limbs of the U-tube are identical. On account of the cooling of the substance in the bulb by evaporation, equilibrium is not reached at once, so that the adjustment has to be repeated until the levels in the U-tube remain constant. The finer adjustment is not easy to manage by the use of the stopcock alone, and the long rubber tube opening to the air is employed. When, for example, a slight increase in pressure is required, the tube is grasped with the hands at two places and air is admitted to the bottle in small portions at a time until equilibrium is attained.

When the adjustment has been perfected, the stopcock on the gage is closed, the temperature reading is confirmed, and the gage and barometer are read. Within the time required for making the gage reading, no variation occurred in the level of the mercury due to a change in temperature in the air confined in the closed limb. To make sure that volatil foreign matter or gas has all been expelled, the whole process of boiling out, adjusting, and reading is repeated until constant values are obtained.

The temperature of the bath is then raised, and a new observation taken. Unless the substance is unstable, and decomposition products arise, repeated boilings at the second and higher temperatures produce no change in the values first obtained.

Section 4. Criticism of the Method.

It will be seen that the isoteniscope is free from the sources of error which affect the older forms of apparatus for determining vapor pressures. For example:

1. The isoteniscope substitutes for mercury a confining fluid of low specific gravity and thus eliminates the error in leveling involved in some static methods.

2. The apparatus dethrones mercury from its position as sole confining fluid, and substitutes a wide choice of liquids. In consequence, all errors due to the volatility of a foreign confining fluid, and to solubility of the substance in, or interaction of, the substance with such a confining fluid disappear entirely.

3. By being adapted to use in a liquid bath (with violent stirring), the apparatus reduces to a minimum all errors due to unsteadiness of the temperature, and to inequality in the temperatures of the substance, its vapor, and the thermometer.

4. By providing a simple method for expelling air bubbles and adhering and dissolved gases, and for repeating the expulsion until the success of the operation is demonstrated, the isoteniscope removes a source of

error (and of total uncertainty as to the amount of that error) which destroys all confidence in the exactness of the results obtained by the older static methods.

5. By permitting the making of an extended series of observations without using more than half of the sample, the apparatus obviates an error due to concentration of involatil impurities in the residue which affects some dynamic methods.

6. By allowing the expulsion of accumulated gas immediately before a reading, the apparatus makes possible accurate measurements with many substances which decompose slowly to give a permanent gas. By the older static methods, accurate measurements in such cases was necessarily impossible.

Aside from this avoidance of certain sources of error, the apparatus possesses some noteworthy advantages:

1. A small amount of material suffices (usually less than 1 gram).

2. The filling of the apparatus, and the manipulations involved in a measurement, are incomparably simpler than any other static method.

3. The correction for dilatation of the bulb of the mercury thermomter (the so-called "pressure" coefficient), which some dynamic methods involve, is avoided

4. Since, with liquids, no foreign substance (such as mercury) is present, the method permits measurements with all reasonably stable liquids, no matter how active, chemically, they may be.

5. The method is applicable to all solids, provided a non-interacting, non-solvent, non-volatil confining liquid can be found. When such a liquid cannot be found, a dynamic method to be described in a later paper ("Studies in Vapor Pressure, V") may be used.

Section 5. The Vapor Pressures of Water.

On account of the facts about water, some of which were brought out in Section 1, namely the ease with which natural impurities are removed, the relatively slight solubilities of gases in water, the more normal behavior of water as shown in the work of Tammann and of Wüllner and Grotian, and the relatively slight inconsistencies in the existing determinations of its vapor pressures, water is a suitable substance for affording a test of the merits of the method. Moreover, no other substance combines all these qualities, and water is therefore at present the only suitable substance.

There is no reason why mercury should not equal, or even excel, water in freedom from impurities and in regularity of behavior. Only the inconsistencies in the measurements which thus far have been made, and especially the utter disagreement of those above the boiling point, render it unsuitable for comparing methods.

Results.—The isoteniscope was thoroughly steamed out, and distilled water, giving no appreciable residue on evaporation, was redistilled into it. The method itself provides for the expulsion of dissolved gases. The measurements were made with the apparatus described above, and the corrections before mentioned were applied.

The observations were made by design as close as possible to temperatures, the values of which should be represented by whole numbers. The differences for one-tenth of a degree at each temperature, taken from Eckholm's[1] tables, were then used in making the very small adjustments required to reduce each observation to the nearest whole number of degrees. The results of this operation are given in the following table (I) under S & M. The pressures in this column, therefore, are not smoothed results, such as may be obtained by graphical or other methods, but are essentially *actual observations*, subject to the irregularities which individual observations usually show. This enables them to afford the most rigorous test of the method, while the adjustment facilitates the comparison with the data of other observers, which are usually given for whole degrees. The twenty-seven observations give, after adjustment, values at eleven different temperatures.

TABLE I.

S & M				Differences, H & H—S & M.	
t.	No. of obsns.	*p.*	H & H.	mm.	Degrees.
50°	3	92.27	92.30	+0.03	—0.006
51	4	97.03	96.99	—0.04	+0.009
55	1	117.87	117.85	—0.02	+0.004
60	2	149.13	149.19	+0.06	—0.010
65	3	187.19	187.36	+0.17	—0.019
70	3	233.44	233.53	+0.09	—0.009
75	1	288.78	289.0	+0.22	—0.018
80	1	354.90	355.1	+0.20	—0.014
85	3	433.54	433.5	—0.04	+0.002
89	5	505.87	506.1	+0.23	—0.011
90	1	525.94	525.8	—0.14	—0.007

For comparison, we give under H & H the corresponding values found by Holborn and Henning[2] in the *Reichsanstalt*. These are undoubtedly the most accurate in existence. Their temperature scale is the same as ours. Their results are smoothed values, derived from numerous observations. The greatest divergencies are 0.23 mm. and 0.019°. The algebraic sum of all the temperature differences, divided by the whole number of our observations (27), gives the mean divergence from H & H's curve of a curve drawn through our observations. This mean divergence is —0.0063°, which is well within the error which we assign to our measurement of absolute temperature (±0.01°). The corresponding mean pressure deviation is +0.08 mm. This agreement is of especial interest since our method is static, while theirs was dynamic.

---

[1] *Svensk. Vet. Akad., Arkiv. för Math., Astron., och Fysik*, Band 4, Häfte 2, No. 29 (1908).

[2] *Ann. Physik*, [4] 26, 833 (1908). The reason for accepting these values as the most accurate will be apparent to any one who considers the details of the method used

Comparison of Other Methods.—We may now institute a comparison between the results obtained by our method and those obtained by others, using Holborn and Henning's values as the standard of comparison.

Taking first the static methods, with which ours may most justly be compared, there are only two sets which included the region 50°–90°, namely those of Magnus and of Batelli. In both cases mercury was the confining fluid, and the U-tube form of vaporizing vessel was used. Magnus[1] boiled the mercury "well" after its introduction. He also boiled the water for 1/2–3/4 hour, and then introduced it, while yet warm, through the open limb, by inclining the apparatus. Batelli[2] "caused the mercury to boil several times." The water was introduced in a small glass bottle, after elaborate purification and subsequent boiling for twenty-four hours. No precautions to remove gases adhering to the small bottles are mentioned.

In the first two columns of the following table (Table II), only the differences between the pressure values of Holborn and Henning and those of Magnus (M) and of Battelli (Ba), respectively, are given. These numbers are to be added to the published data, to give those of H & H. The other columns will be explained presently:

TABLE II.

(Differences from H & H.)

	Static.		Dynamic.		Recalculations.		
t.	M.	Ba.	Rg.	W.	Br.	T.	E.
50°	+0.33	+1.85	+0 28	...	+0.32	—0.22	—0.34
60	+0.61	+2.3	+0.36	...	+0 31	—0.19	—0.38
70	+0.92	+2.7	+0.58	...	+0.22	—0.14	—0.40
80	+1.2	+2.7	+0.5	—0.3	+0.2	0.0	—0.34
90	+1.0	+2.1	+0.3	—0.2	+0.3	0.0	—0.2
Av.	+0.81	+2.3	+0.4	—0.25	+0.27	—0.11	—0.33

The average divergencies from H & H are: Magnus +0.81 mm. (or —0.07°), Batelli +2.3 mm. These are respectively ten and thirty times as great as our average divergence. It must be noted that the data of these two observers are all smoothed values.

Schell and Heuse[3] have recently determined the value at 50° (92.54 mm.) by a static method. Our value (static) confirms that of H & H.

---

[1] *Pogg. Ann.*, 61, 225 (1844).

[2] *Ann. chim. phys.*, [6] 26, 410 (1892); [7] 3, 408 (1894).

[3] *Ann. Physik*, [4] 31, 715.

On account of the extensive use which has been made of Ramsay and Young's static methods, both by themselves and by others, a comparison would be very instructive. Their barometer tube method, available up to nearly 760 mm., with the special device for filling so as to exclude foreign gases, was not applied to water, which is the only suitable substance for making a rigid comparison. Their only determinations with water[1] begin at 120°, and are therefore not directly comparable with ours. The filling of the tube[2] involved boiling of the substance, but not of the mercury in the tube. The differences between their values and those of H & H at their lowest temperatures are as follows: 120°, +4.9; 130°, +6.6; 140°, +15.5; 150°, +0.7. The average divergence is +6.9 mm., or —0.1°, and is of the same order as that of Magnus. These, again, are smoothed values. This divergence is not due to the difference between the scales of temperature used by Ramsay and Young (const.-vol. air-therm.) and by H & H, for this would not exceed 0.014° (corresponding to 1.3 mm.) even at 150°, and besides, if taken into account, would increase the divergence.

If we turn now to results obtained by dynamic methods, there are only three sets which include the region under consideration, namely those of Regnault, Wiebe (82°–100°), and Holborn and Henning. Regnault's[3] dynamic observations extended from 43° to 230°. In the column headed Rg of the foregoing Table II, we give the differences between the data of H & H and of Regnault, using for the latter the data calculated by the "H" formula. This was the formula which Regnault found most generally satisfactory, and it appears to be especially so within the region in question. Wiebe[4] made measurements from 82° to 100° only. His results (Col. W), however, seem to be considered especially good by H & H, and they are weighted very heavily in Eckholm's recalculation of the data which he considered. The average divergences from the results of H & H are: Regnault, +0.4 mm. (or —0.04°), and Wiebe —0.25 mm.

On account of the very large number of measurements made by Ramsay and Young, and by other observers, with their dynamic method,[5] in which the thermometer bulb is surrounded by cotton saturated with the substance, a comparison of its performance with that of other methods is extremely desirable. Unfortunately, although they made a series of observations with water,[6] they give no results and content themselves with stating that the values were "identical with those of Regnault."

---

[1] *Phil. Trans.*, *A*, **183**, 107 (1892).

[2] *Ibid.*, *A*, **178**, 57 (1886); Young, *Stoichiometry*, 134 (1908).

[3] *Rel. des Experiences*, **1**, 465 (1847).

[4] *Z. Instrumentenkunde*, **13**, 329 (1893).

[5] See Section 2 of this paper.

[6] *Phil. Trans.*, **175**, 48 (1884).

It is a pity that they did not state more exactly the degree of approximation, and specify which of the appreciably divergent sets of data were used in the comparison—for example, the curve, the values calculated by "formula H" (those most commonly quoted, *e. g.*, in the *Chemiker Kalendar* and Van Nostrand's *Chemical Annual*), or Brock's recalculation (adopted by Ostwald in his *Handb.*). As we have seen, however, the method is open to serious criticism.

Finally, in the last three columns (Table II) we give the results of Regnault, as recalculated by Brock (Br), the data of all previous observers as combined and recalculated by Thiesen[1] (T), which were adopted without change up to 100° by Henning[2] in his most vigorous study of the same data, and the results of Eckholm's (E) recalculation of the same data. As before, only the differences, H & H—Br, etc., appear.

This comparison shows that, assuming Holborn and Henning's values to be correct, the results by our method lie much closer to the true value than do those by any other static method. They likewise diverge much less than do the results of the recalculations of previous determinations. They lie also much closer than do the values obtained by the dynamic methods, although all writers are agreed that the dynamic methods give more trustworthy results than do the static ones which have hitherto been employed.[3]

The degree of self-consistency of the observations may be seen by inspection of Table I. A more detailed study of the deviations from a smooth curve of the individual observations obtained by this method will be undertaken in the following paper on mercury.

To determin definitly the merits of the isoteniscope, *per se*, it would be necessary to eliminate from the older observations the effects of the errors in the measurements of temperature and of pressure, and to isolate the error due to the form of the vaporizing chamber and the method of handling the substance. It is unfortunately impossible to do this. It is to be noted, however, that the gage and thermometer errors are common to static and dynamic methods, and should be essentially alike in both. Now the average magnitude of the divergencies of the dynamic and static methods, respectively, from that of H & H are 0 33 mm. and

---

[1] *Ann. Physik*, [3] 67, 692 (1899).

[2] *Ibid.*, [4] 22, 609 (1907). This was before the redetermination by Holborn and Henning.

[3] The much closer approximation of our results to those of H & H is not due to the fact that the same scale of temperature was used by both, whereas the other observers used air thermometers (Regnault, a mercury thermometer). The difference between the scales at 50°–90°, except possibly in the case of Regnault's values, is so small that it would equal only a fraction of the divergence in each case, and besides, wherever the differences in pressure are positive in the preceding tables, an adjustment to the thermodynamic scale would only increase the divergencies.

1.55 mm. The excess of the static over the dynamic may perhaps be held roughly to represent the minimum value of the error of the older static methods *per se*. Now this difference is 1.22 mm., or about fifteen times the total divergence of our results due to all causes.

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

STUDIES IN VAPOR PRESSURE: IV. A REDETERMINATION OF THE VAPOR PRESSURES OF MERCURY FROM 250° TO 435°.

BY ALEXANDER SMITH AND ALAN W. C. MENZIES.

Received August 20, 1910.

Both for practical and theoretical purposes, an exact knowledge of the physical constants, and particularly of the vapor pressures of mercury, is of the greatest importance. Mercury is used in innumerable ways in research and in many instances the accuracy of the results depends on a knowledge of the vapor pressures of this substance. Since mercury shows no evidence of a tendency to association, and since its vapor is monatomic, presenting in the former respect a great contrast to water, and in the latter respect even to the liquids of more normal behavior, like benzene, an exact knowledge of its vapor pressures should be of the utmost value in the study of the laws pertaining to vaporization. The relations, for example, between temperature and pressure and between these two and heat of vaporization, on account of the absence of complicating factors, should be of special simplicity in the case of mercury. Moreover, it is more easily obtained in a state of extreme purity than almost any other substance. Yet, in spite of all this, as Laby says, "the greatest—and it should be added, unnecessary—disagreement is to be found in the current values of this vapor pressure." For these reasons, and because accurate data were required for a study of calomel vapor which will shortly be published, a redetermination of the vapor pressures from 250° to 435° was undertaken. The range chosen was limited to the region required for this special purpose, but we intend later, with a longer gage, to extend the series. The theoretical study of our results is postponed until the longer series shall be available.

Previous Determinations.—The work of previous observers has been subjected to a critical study and their data have been combined by Laby.[1] We are not concerned with the values at low temperatures, of which those of Pfaundler,[2] Morley,[3] and Hertz[4] (the latter's extend to 207°) are in excellent agreement, and are irreconcilable with the erratic values of

---

[1] *Phil. Mag.*, [6] 16, 789 (1908).

[2] *Ann. Physik*, [3] 63, 36 (1897).

[3] *Phil. Mag.*, [6] 7, 662 (1904).

[4] *Ann. Physik*, [3] 17, 193 (1882)

Van der Plaats,[1] Hagen,[2] and McLeod.[3] As regards Regnault's[4] three low-temperature series, including observations up to 205°, he himself states that they give data that are only approximate. The series of determinations discussed below are those which touch the region covered by our experiments. The data themselves will be found in a comparative table (Table VI) given towards the end of the paper.

Regnault's values at the highest temperatures are based, (1) on four old determinations of the boiling point of mercury (about 357°) made with an air thermometer, two of which differ by about 2° at the same pressure, and (2) a new series from 251° to 511.7°. In the latter, the mercury boiled under varying air pressures. The temperatures were determined with a constant-volume air thermometer. The boiling metal began to bump occasionally at 345° and violently at 428°. The values near the ordinary boiling point are obviously discordant, as the three following observations show: 354.60°, 758.20 mm.; 354.83°, 761.87 mm.; 356.69°, 754.43 mm. Later workers have made much of Regnault's statement that his results were inaccurate, but he makes no such admission in regard to these two sets of values, leaving them to speak for themselves. All he says is that the experiments were not done in the same way as those which he made with other substances, because, when the bulb of the thermometer was surrounded by vapor, constant temperatures could not be obtained, and in this case, therefore, the bulb was completely below the surface of the liquid. Owing to the great depth of the mass of mercury (50 kilos), the lowest layers must have been seriously superheated.

Ramsay and Young's[5] well-known series of vapor pressures of mercury was based upon four groups of observations. Young, in a paper which appeared five years after and seems to have escaped notice,[6] utilized later values for a part of the fundamental data, and gives a corrected and very considerably altered table (see Table VI). The four original groups of observations were:

1. Four static measurements with mercury in a U-tube[7] heated by the vapor of methyl salicylate boiling at a known pressure. The temperature of the vapor was ascertained indirectly from a previously determined p.-t. curve. This p.-t. curve not having given satisfactory

---

[1] *Rec. trav. chim.*, 5, 149 (1886).

[2] *Ann. Physik*, [3] 16, 610 (1882).

[3] *Brit. Assoc. Rep.*, 1883, 443.

[4] *Mem. Acad. Sci.*, 21, 30, 502 (1847); 26, 506 (1862).

[5] *J. Chem. Soc.*, 49, 37 (1886).

[6] *J. Chem. Soc.*, 59, 629 (1891). Not referred to in Landolt and Börnstein, [3] (1905), nor in Abegg's *Handb.*, II, ii (1905), which give the old set of values.

[7] For proof of the difficulty in excluding foreign gases from such a tube see preceding paper, Sec. 2.

results in other cases, Young, in the second paper, discards these observations and substitutes for them two new readings with aniline vapor as the heating agent at 183.7° and one with quinoline vapor at 236.9°. These temperatures (const.-vol., air-therm. scale) are therefore ascertained indirectly as before.

2. Two static measurements with mercury in a U-tube heated by the vapor of bromonaphthalene boiling at known pressures. It is a little difficult to make out the exact status of this part of the data. These were old observations, originally made as part of a study of the vapor pressures of bromonaphthalene.[1] On that occasion, the temperature corresponding to the observed bromonaphthalene pressure was ascertained by taking from Regnault's formula the temperature at which mercury exercised the vapor pressure observed in the U-tube. These, along with three other series of measurements made in a different way, were employed in making the bromonaphthalene p.-t. curve. They entered directly into the making of the curve, and were used also for ascertaining the correction of an English thermometer employed in one of the other (the fourth) series.

On the present occasion they play the reversed roles of measurements of the vapor pressure of mercury. One of these agrees with the final p.-t. curve of bromonaphthalene and the other is adjusted by altering the temperature 0 4° to bring it onto this curve. As these results are retained and used by Young in the second paper, it is necessary to consider their probable accuracy.

The values, as adjusted, were considered to be correct for two reasons. One was because they gave normal results when used in the study of certain vapor pressure relations of water and bromonaphthalene, expressed by the formula $R' = R + c\ (t'-t)$.[2] But water is an abnormal substance and is admitted to be unsuitable for the study of this relation,[3] so that the agreement of the results with the theory in this instance affords no guarantee of the accuracy of the data. The vapor pressures of mercury adopted on the basis of this observation, when compared with those of water in the light of the same relation, again showed good, but, for the same reason as before, unavailing agreement with the theory. The value of the results must be judged, therefore, solely by the other reason for considering them correct, namely, the accuracy of the p.-t. curve of bromonaphthalene on which they are based.

This curve[4] is founded on several series of observations. Two series were made by Ramsay and Young's dynamic method,[5] in which the thermometer bulb is surrounded by cotton and immersed in the vapor. No correction for dilatation of the bulb[1] is mentioned, but its absence would not affect the results at 280°, with which we are concerned, as the pressure is there atmospheric. The objections on account of the introduction of dissolved gases along with the liquid, and of the gradual concentration of impurities, however, still remain. The results of the second series are below those of the first by 0.8° at 278°. In the fourth series, the bromonaphthalene boiled in a tube under known pressures and its temperature was ascertained by means of a thermometer immersed in the vapor. This was the thermometer standardized by assuming Regnault's vapor pressure curve of mercury to be correct. The results are above those of the second series at 280° by 1.9°. The temperatures in these series were all reduced to the constant-volume, air-thermometer scale. The third series consisted of the pair of observations first referred to.

---

[1] *J. Chem. Soc.*, 47, 65 (1885).

[2] *Phil. Mag.* [5], 20, 515 (1885); 21, 33 (1886).

[3] Young, *Stoichiometry* (1908), 144.

[4] *J. Chem. Soc.*, 47, 646 (1885).

[5] For detailed criticism see preceding paper, Sec. 2.

It appears, therefore, that these two observations are not independent of the p.-t. curve of bromonaphthalene, and that the latter is made from data diverging as much as 1.9° at 280°.

In a later paper, Young[2] refers to certain discrepancies in results obtained by the use of the p.-t. curve of bromonaphthalene vapor, which he believes to be due to a slight underestimation of the temperatures at 280°. Table IV, however, will show that these two sets of observations from 183.7 to 280° are probably much more accurate than those of Hertz in the same region.

3. The third group of data pertaining to the vapor pressures of mercury used by Ramsay and Young consisted of the four boiling points of mercury originally employed by Regnault, two of which differed by 2° at the same pressure. Young, in the later paper, rejects these and substitutes Callendar and Griffiths'[3] determination of the boiling point of mercury at 760 mm., reduced to the sea level at latitude 45°, the value of which is generally quoted as 356.76° (const.-press. air-therm. scale). In this work, the details of which cannot be discussed here, the authors used values obtained with four improved platinum resistance thermometers, each compared in the vapor of boiling sulphur and at 0° and 100° with a constant-pressure air-thermometer. The mean result, reduced to the basis of the S b. p. = 444.53°, which the same observers had determined, was 356.76°. The mean of the results with five earlier, trial platinum thermometers, similarly reduced, was 356.74°. A final set of three "very careful" observations with a new platinum thermometer gave the mean value 356.73°. The final mean value with the five best ther-

---

[1] This Journal, 32, 905.

[2] *J. Chem. Soc.*, 77, 1147 (1900)

[3] *Phil. Trans.*, *A*, 182, 150–2 (1891).

mometers is 356.74°, in exact agreement with that of the five earlier instruments.

4. The fourth, and last, of the groups of observations used by Ramsay and Young consisted in two static measurements of the vapor pressure of mercury when heated by boiling sulphur. For the temperature, Regnault's boiling point of sulphur, 448.34°, the only one then available, was used. Young retains the pressure data and substitutes Callendar and Griffiths'[1] value for this boiling point (444.53°). According to Ramsay and Young's table, a difference of 4°, such as this, corresponds to a change in pressure at 445° of 139 mm. Hence this substitution greatly altered the value at 445°, as well as all the values between 760 and 2850 mm., which, in the absence of intermediate determinations, were all obtained by interpolation.

The vapor pressures were determind by heating the mercury in an apparatus shaped like a round-bulbed thermometer, with the stem bent into a horizontal position. The mercury, when cold, filled the bulb and a part of the stem, and was driven along the latter, compressing the air in the end, when mercury vapor was formed in the bulb. The bulb and a portion of the non-horizontal part of the stem of this thermometer-shaped apparatus were surrounded by the vapor of sulphur boiling in a vessel which in one experiment was a flask and in the other a wide test tube. Dr. Young, whom we desire to thank for most courteously giving us additional information on a number of points, states that the air column, before compression, was approximately 400 mm. in length. At four atmospheres pressure its length was thus reduced to 100 mm. Since the reading was probably accurate to ±0.1 mm., the pressure error should be only ±1 in 1000, or about 3 mm. The accuracy of the pressure reading was therefore satisfactory.

It is unquestionable, however, that in assuming that the bulb was really heated to 444.53° by the arrangement used, a serious error is introduced. The flask and test tube containing the boiling sulphur were not covered or protected in any way. Now, Callendar and Griffiths devote much space in their paper to a detailed description of their observations on this point. They used a Victor Meyer vapor density tube 4 cm. in diameter. Even when such a tube was padded externally with asbestos to retain the heat, the temperature reached by the thermometer was only 442.38°. They showed that the temperature of their thermometer (corresponding in Ramsay and Young's experiment to the bulb) was reduced by the trickling down of condensed, cooled sulphur and by radiation to the layer of condensed sulphur on the walls. By introducing a little hood to divert the sulphur running from the stem, and two cylindrical screens (one of metal and one of glass) to stop radiation, they finally brought the observed temperature up to 444.53°. In Ramsay and Young's experiment, therefore, the temperature actually reached was probably not far from 442.38°, or about 2° short of the value assigned to it by Young.

---

[1] *Phil. Trans.*, *A*, 182, 119 (1891). See also preceding paper, Sec. 3.

Gebhardt[1] boiled mercury in a glass globe. The temperatures of the vapor were taken with "a thermometer," presumably a mercury thermometer. No attempts to standardize the instrument, or to correct the readings for exposed thread or dilatation are described. Corrections of the gage are likewise lacking. But the pressures are given to tenths of a millimeter (see Table II).

Cailletet, Colardeau, and Rivière[2] determined, by a static method, the vapor pressures in atmospheres from 400° to 880°. The results are of interest as showing the order of the pressures at very high temperatures. The authors state that their results are sensibly the same as Regnault's, so far as the latter extend. Laby used these results although he rejected Regnault's, and this accounts for the fact (see Table VI) that above 360° his figures are higher than those of Young. No information as to the values assumed for the fundamental points, or as to the scale of temperature employed, is given.

Summarizing the history of this subject, we find that our knowledge of the higher vapor pressures of mercury rests on no very secure foundation. The boiling point at 760 mm. is the only point ascertained with precision. Not one observer makes any statement in regard to the purity of his mercury. Aside from Callendar and Griffiths, Regnault is the only investigator who states what he did in every experiment with perfect lucidity and completeness. Unfortunately, his results at closely adjacent points are inconsistent, his temperatures are those of the liquid and not of the vapor, and his air thermometer was inexact in its readings.

The Vapor Pressures of Mercury.—The apparatus used was identical with that described in the preceding paper.[3] The U-tube of the static isoteniscope contained mercury. The mixture of potassium and sodium nitrates was used as the bath liquid. The vibration communicated from the stirrer prevented bumping, which otherwise might have occurred when the metal in the bulb was allowed to boil.

The mercury, already distilled *in vacuo*, was redistilled in the same way at the rate of 30 cc. per hour. It was then washed ten times with dilute nitric acid in a tube 1.3 meters long, by the method recommended by Hildebrand.[4] This method is like Ostwald's excepting that the metal is strained through muslin, which divides it into extremely small streams, instead of being allowed to enter the acid in a single stream. It was then dried and tested by the method of Hulett and Minchin,[1] which is incomparably the most sensitive. A portion of the metal was distilled twice in air, which oxidizes the more active metals, if present. Samples of each lot were then placed in a cell containing *N* KCl solution saturated with calomel. The potential difference of the two samples was less than 0.000002 volt, the limit of sensitiveness of the galvanometer employed. The method is capable of detecting one part of zinc in 10^{10} parts of mercury, and corresponding amounts of other active metals. The mercury in the gage was also tested and found to be of a like degree of purity.

---

[1] *Ber. physik. Ges.*, 7, 184 (1905).

[2] *Compt. rend.*, 130, 1585 (1900).

[3] THIS JOURNAL, 32, 1419.

[4] *Ibid.*, 31, 933 (1909).

The corrections and the precautions, such as frequent redeterminations of the fixed points, were identical with those used in the observations with water which are recorded in the preceding paper.

Two series of readings, hereafter named the first and second series, were completed. In the first attempt to make the second series, the isoteniscope broke after the fourth reading. Since the next, and successful second series overlapped the first series for a considerable distance, rendering the four observations in the same region unnecessary, and since the instrument may have been defective before the breakage occurred, the four readings of the abortive series were not used. Aside from those four, every observation that was completed is recorded in Table I. The results, 43 in all, are given in the order of ascending temperatures, in which they were obtained. The members of the second series are distinguished by an asterisk.

It may be noted that an alteration in the zero of the thermometer, requiring a change of about 0.1°, occurred between the first and second series. On account of the overlapping, however, the individual observations are affected only to the extent of 0.05°. The aim was to secure observations with a temperature error of less than ±0.1°. The temperatures are worked to hundredths of a degree as, although not accurate to one unit in this place, the second decimal has nevertheless some significance.

The temperatures are on the thermodynamic scale, and assume the boiling point of sulphur to be 445° on that scale. If, later, a slightly different value for this point should be finally accepted, the preceding paper supplies the data required for any recalculation. If the S b. p. is taken 0 1° lower (*i. e.*, 444 9°), which is the present most probable value, then at 357°, for example, a correction of —0.06° is required.

The error of the individual gage readings, considered by themselves, is less than ±0 2 mm. The pressures are given to hundredths, although the second place has very little significance.

---

[1] *Physic. Rev.*, 21, 388 (1905).

Critical Study of the Results.—The observations were first plotted on a large scale, equivalent to a piece of cross-section paper 118 x 220 cm., and a smooth curve was drawn through them. This made easy the selection of three points, from which a Kirchoff-Rankine-Dupré formula was calculated. From this formula the pressures at every 2° in the region studied were reckoned. By linear interpolation, which is sufficiently accurate for intervals of 2°, the calculated temperatures corresponding to the observed pressures were then obtained. A study of the divergencies of the calculated and observed temperatures now showed that an alteration in two of the fundamental points would cause the formula better to fit the observations as a whole. With the very slightly altered points the whole process was repeated, and a further slight change in all three points was made. Thus, after two approximations, a final set of three points and a corresponding formula of a very satisfactory nature were secured. The fundamental points on which the final formula is based are:

264.16°, 106.52 mm., 356.95°, 760 mm.; 433.96°, 2598.67 mm.
The formula is $\log p = A + B/\theta + C \log \theta$, or, with the constants inserted:

$$\log p = 9.9073436 - 3276.628/\theta - 0.6519904 \log \theta, \qquad \text{(R)}$$

where $\log B = 3.5154272$; $\log C = \bar{1}.8142412$.

The following table contains. the reference numbers of the experiments (Col. 1), arranged in the order of ascending temperatures, with those of the second series distinguished by an asterisk; the observed pressures (Col. 2); the observed temperatures (Col. 3); the temperatures calculated with the use of the formula by the process indicated above (Col. 4); and the differences (Δ) between the observed and the calculated temperatures.

If the formula fitted the observations exactly, the algebraic sum of the divergencies should be zero. It is actually +0.07°. A change of 0.003° in the middle point might improve the correspondence, but it did not seem desirable at present to attempt any such refinement.

Since the calculated temperatures lie on a smooth curve, the divergencies from them of the observed temperatures represent essentially the irregularities in the individual observations. A study of column 5 will, therefore, show the degree of consistency of the results. Of the forty-three observations, thirty show very small deviations, ranging from 0.00° to 0.05°. In eight cases the divergence is from 0.06° to 0.10°, in only five cases does it exceed 0.10°. Observation No. 37 is undoubtedly defective, on account of a misreading of the resistance or of the gage. The mean deviation from the smooth curve of a single observation (including No. 37) is 0.050°. This is well within the limit proposed for the accuracy of the absolute temperature measurements.

TABLE I.—THE OBSERVATIONS.

No.	Press obsd.	Temp. obsd.	Temp. calc.	Δ.	No.	Press. obsd.	Temp. obsd.	Temp. calc.	Δ.
1	82.08	253.97	253.91	—0.06	23	747.81	355.98	356.05	+0.07
2	96.84	260.35	260.36	+0.01	24	765.44	357.32	357.34	+0.02
3	106.52	264.16	264.16	0.00	25*	769 26	357.72	357.62	—0.10
4	117.04	267.99	267.96	—0 03	26	817.00	361.04	360.99	—0 05
5	128.57	271.82	271.81	—0.01	27*	836.43	362.43	362.32	—0.11
6	141.05	275.68	275.66	—0.02	28*	885.76	365.62	365.58	—0.04
7	169.82	283.61	283.55	—0.06	29*	932.66	368.54	368.55	+0.01
8	210.79	293.07	293.04	—0.03	30*	1002.55	372.74	372.74	0.00
9	236.96	298.34	298.31	—0.03	31*	1008.68	378.66	378.69	+0.03
10	273.24	304.75	304.86	+0.11	32*	1210.58	383.95	383.99	+0.04
11	309.73	310.75	310.77	+0.02	33*	1265.60	386.66	386.69	+0.03
12	334.92	314.33	314.51	+0.18	34*	1326.12	389.56	389.56	0.00
13	428.93	326.65	326.69	+0.04	35*	1425.97	394.04	394.07	+0.03
14	457.10	329.87	329.91	+0.04	36*	1675.34	404.28	404.32	+0.04
15	498.01	334.16	334.30	+0.14	37*	1744.34	407.17	406.94	—0.23
16	537.55	338.21	338.27	+0.06	38*	1847.35	410.66	410 69	+0.03
17	586.76	342.82	342.88	+0.06	39*	2037.15	417.17	417.19	+0.02
18*	635.00	347.13	347.11	—0.02	40*	2125.78	420.10	420.07	—0.03
19	642.22	347.74	347.72	—0.02	41*	2334.34	426.52	426.47	—0.05
20	697.73	352.13	352.23	+0.10	42*	2599.17	434.02	433.95	—0.07
21*	697.72	352.24	352.23	—0.01	43*	2624 35	434.71	434.65	—0.06
22	732.13	354.85	354.87	+0.02					

Comparison with Other Methods.—The qualities of the method used are best seen by applying the same mode of study to the observations of other observers. Cailletet, Colardeau, and Rivière do not publish their observations, but only the rounded results. Ramsay and Young's observations are not numerous enough for the purpose. Only in the cases of Regnault and Gebhardt[1] can the data be investigated as regards their consistency. In the following table (Table II) the observations of Gebhardt (taken from Laby's paper, as the dissertation is not accessible) are given. It contains the observed pressures (Col. 1), the observed temperatures (Col. 2), the temperatures calculated by the use of formula R (Col. 3), and the differences (Δ_1) between the temperatures as observed and as thus calculated (Col. 4). The algebraic sum of these deviations divided by the number of observations is +0.81°, showing that the observed temperatures are on the whole 0.81° below those calculated.

A curve was drawn fairly to represent his results, and the divergencies of the individual observations from this curve are given under Δ_2 (Col. 5). The sum of these divergencies is +0.2°, that is, approximately zero, as it should be. It will be noted that the individual temperatures, besides being, as we have seen, on the whole 0.81° too low, are exceedingly irregular. The mean deviation of a single observation from the smooth curve is 1.2°, or about twenty-four times as great as in the case of the present observations. The method is, in part, responsible for this.

---

[1] *Loc. cit.*

TABLE II.—GEBHARDT'S OBSERVATIONS

Press obsd	Temp. obsd.	Temp. calc	Δ_1	Δ_2.	Press obsd	Temp obsd	Temp calc	Δ_1.	Δ_2
1.00	129.0	126.0	3.0	-3.8	94.40	256.0	259.3	+3.3	+2.5
3.93	157.5	158.4	+0.9	+0.1	105.69	264.0	263.8	-0.2	1.0
8.22	176.5	178.2	+1.7	+0.9	122.90	268.0	270.0	+2.0	+1.2
12.51	188.0	190.3	+2.3	+1.5	126.11	271.5	271.0	0.5	1.3
21.07	207.0	206.3	0.7	1.4	150.80	277.5	278.4	+0.9	+0.1
38.82	224.5	226.6	+2.1	+1.3	147.50	278.5	277.5	-1.0	-1.8
46.49	230.5	232.9	+2.4	+1.6	185.00	286.5	287.3	+0.8	0.0
51.58	236.0	236.6	+0.6	0.2	224.90	295.5	295.9	+0.4	-0.4
68.4[illegible]	245.0	247.0	+2.0	+1.[illegible]	263.90	302.5	303.3	-0.8	-1.6
71.39	248.0	248.6	0.6	0.2	308.10	309.5	310.2	0.7	1.5
87.87	255.0	256.5	+1.5	0.7	360.[illegible]	315.0	318.1	+3.1	+2.3

Regnault's main series (251° to 512°) is exhibited in Table III. Col. 3 contains the temperatures calculated by our formula, and Col. 4 the differences between the temperatures as observed and as thus calculated. The mean deviation of a single observation is 2.84°. Col. 5 shows the temperatures as calculated by Regnault's own formula (shorter form) and Col. 6 the differences between the temperatures as observed and as thus calculated. The mean deviation of a single observation from the smooth curve represented by Regnault's formula is 3.29°. Our formula thus fits his results better than does his own. The character of his work on this subject hardly justifies the extent to which his results have been quoted and used. It must be remembered, however, that he does not discuss their exactness, much less claim for them any special accuracy.

TABLE III.—REGNAULT'S OBSERVATIONS

Press obsd	Temp obsd	Temp calc (S & M)	Δ_1	Temp calc (Reg.)	Δ_2
74.10	251.08	250.00	1.08	249.15	1.93
78.10	252.60	252.00	0.60	251.26	1.34
85.10	255.45	255.30	0.15	254.71	0.74
238.38	297.21	298.14	-0.93	299.28	-2.07
345.80	314.06	316.02	-1.96	316.88	-2.82
486.31	331.60	333.07	-1.47	333.83	+2.23
624.90	344.80	346.25	-1.30	346.84	+1.95
761.87	354.83	357.09	-2.26	357.48	+2.65
758.20	354.60	356.82	+2.22	357.22	+2.62
1529.60	412.96	398.50	14.46	397.70	-15.26
2086.2	428.35	436.31	-7.96	433.96	+5.61
3180.6	444.06	448.51	+4.45	445.62	+1.56
4613.8	475.73	476.01	-0.28	472.74	—2.99
7316.7	511.67	515.75	+4.08	509.58	—2.09
6990.1	508.53	511.72	+3.19	505.75	—2.78
5966.2	499.88	498.13	—1.75	492.79	—7.09
754.43	356.69	356.54	-0.15	356.95	+0.26

Comparison of all Observations.—Since it thus appears that the present observations are probably of a relatively high order of accuracy, it is instructive to compare the results of other observers. In the following tables are given all the published observations, omitting those of Regnault and most of Gebhardt's. The initials are those of the observers: Young (Y), Ramsay and Young (R Y), Hertz (H), Callendar and Griffiths (C G), Cailletet, Colardeau, and Rivière (C C R), Pfaundler (P), Morley (M).

In the first table (Table IV) appear the observations above 200°, with two others, and also the rounded values of C C R (no observed data having been published by them). Since in this region the chief experimental error lies in the measurement of temperature, rather than of pressure, the comparison is made in the same way as before.

TABLE IV.—OTHER OBSERVATIONS, CHIEFLY ABOVE 200°.

Obsr.	Press obsd	Temp obsd	Temp calc	Δ
Y........	9.94	183.8	183.62	−0.18
Y........	9.85	183.7	183.35	−0.35
H.....	20.35	203.0	205.29	+2.29
H..........	22.58	206.9	208.56	+1.66
Y	51.85	236.9	236.78	−0.12
RY..... . ..	124.35	270.35	270.43	+0.08
R Y...	157.15	280.2	283.23	+0.03
C G....	760	357.08	356.95	−0.12
C C R.	1596	400	401.00	+1.00
R Y–Y .. .	2896.90	443.15	441.71	−1.44
R Y–Y	2904.50	444.15	441.92	−2.23
C C R.......	3230	450	449.65	−0.35
C C R...	6080	500	499.7	−0.3
C C R.	10488	550	549.0	−1.0
C C R....	16948	600	599.4	−0.6
C C R......	25840	650	647.1	−2.9
C C R....... . .	38000	700	696.3	−3.7
C C R......	77520	800	804.6	+4.6
C C R............	123120	880	889.6	+9.6

Callendar and Griffiths' value is the mean of all their boiling-point observations reduced to thermodynamic temperature (S b. p. = 445°). None of the other temperatures have been reduced. At the high temperatures (C C R), where the reduction would make the most difference, no data are furnished by the authors. The values of the temperatures near 443–444° (Young) are about 2° too high, for the reason already given.

Table V contains all the observations below 200°. Since in this region the pressures are very low, the chief errors affect the pressures rather than the temperatures. In this table, therefore, the observed pressures (Col. 3) are compared with those calculated by formula R (Col. 4). The differences are given in column 5, and in column 6 is stated the percentage of the calculated value which was observed (*i. e.*, calculated value = 100).

TABLE V.—OBSERVATIONS BELOW 200°.

Obsr.	Temp obsd	Press. obsd	Press. calc.	Δ.	Percentage.
P........	15	0.00081	0.000844	+0.000034	96.0
M........	16	0.0010	0.000922	−0.000078	108.5
M	30	0.0027	0.00298	+0.00028	90.3
M	40	0.0052	0.00648	+0.00128	80.2
M........	50	0.0113	0.01339	+0.00209	84.4
P	56.3	0.01807	0.02068	+0.00267	87.1
M	60	0.0214	0.02648	+0.0050	80.8
M	70	0.0404	0.0529	+0.0125	76.4
H	89.4	0.16	0.1575	—0.0025	101.6
P........	98.8	0.26305	0.26220	—0.0008	100.3
H	117	0.71	0.6552	−0.0548	108.4
G.... ...	129	1.000	1.144	+0.144	87.4
H . ..	154.2	3.49	3.3280	—0.162	104.9
G	157.5	3.93	3.718	—0.212	105.7
H . ..	165.8	5.52	5.216	—0.304	104.3
G. . ..	176.5	8.22	7.732	—0.488	106.4
H	177.4	8.20	7.985	—0.215	102.7
R Y ...	183.4	9.87	9.8670	—0.003	100.0
H	184.7	11.04	10.322	—0.718	107.0
G . .	188	12.51	11.560	—0.95	108.2
H .	190.4	12.80	12.540	−0.35	103.0

Morley's results were obtained by saturating carbon dioxide with mercury vapor. The calculated values seem to represent the results as a whole fairly well.

TABLE VI.—COMPARATIVE TABLE OF ROUNDED RESULTS.

Temp	Reg	R & Y	Y.	G	Laby	S & M.
255°	85.9	85.0	...	....	86.2	84.45
260	96.7	96.7	96.5	100.0	97.8	95.94
270	123.0	123.9	124.0	120.0	124.8	123.02
280	155.2	157.4	157.8	158.8	158.4	156.29
290	194.5	198.0	108.9	199.5	199.3	196.81
300	242.2	246.8	248.6	249.0	248.6	245.85
310	299.7	304.9	308.0	309.0	307.7	304.69
320	368.7	373.7	378.5	..	378.1	374.82
330	450.9	454.4	461.7	.	461.3	457.85
340	548.4	548.6	559.1	.. .	559.1	555.54
350	663.2	658.0	672.5	.	673.3	669.77
360	797.7	784.3	803.7	....	805.9	802.62
370	954.7	930.3	954.7	.	959.2	956.25
380	1140	1096	1228	C C R	1135	1133.0
390	1347	1284	1325	. ...	1337	1335.4
400	1588	1496	1549	1596	1566	1566.1
410	1864	1734	1801	....	1826	1827.6
420	2178	2000	2085	....	2119	2123.4
430	2533	2299	2403	....	2446	2456.0
435	2728	2459	2572	....	2628	2637.5
440	2934	2629	2757	....	2817	*2828.8*
445	3153	2808	2939	....	3018	*3031.5*
450	3384	2996	3150	3230	3229	*3245.0*

The preceding comparative table (Table VI) gives the smoothed results of various observers, for the most part for every ten degrees. It comprises only the region of the present experiments, with an extension of 450°, to include the boiling point of sulphur and two values by C C R. The values under S & M are calculated from formula R, and those which are extrapolated are in italics. Laby's recalculation took into account all the preceding data, excepting those of Regnault. But it will be seen that, above 340° at least, the errors in the latter are not as great as was at first suspected.

The Boiling Point of Mercury.—As considerable interest attaches to the knowledge of the exact boiling point of mercury at 760 mm., the values found for that point by different observers may be compared.

Regnault made seven measurements close to this point. The mean, when the results are reduced to 760 mm. and to thermodynamic temperature[1] (S b. p. = 445°), and when all are given equal weight, is 357.7°. The average deviation of a single observation from this mean is 1.34°.

Callendar and Griffiths' result with the five best thermometers, giving equal weight to each determination, is 356.74°. The correction to the thermodynamic scale (S b. p. = 445°) is about +0.34°, making the value 357.08°, with an average deviation of the individual observations from this mean of 0.02°. They believe that their absolute temperature measurement is correct ±0.1°. In judging of the probable accuracy of this value it is to be noted that they heated their mercury at the bottom with a small flame. The layer from which the vapor proceeded was therefore under a head of mercury indicated by the scale of their drawing to have been about 53 mm. The vapor was therefore probably superheated, and no mention is made of experiments to ascertain whether lowering or raising the thermometer altered the value of the observed temperature. We should expect, therefore, that their temperature would be, if anything, too high.

The present value, from the formula, is 356.95°, with the absolute temperature measurement believed to be accurate to ±0.1°. The possibility of superheating is here eliminated.

Table of Smoothed Results.—Finally, a table (VII) of the vapor pressures of mercury for every two degrees from 0° to 458°, calculated by formula R, is given. The extrapolated values, below 255° and above 435°, are in italics. The values below 255° probably represent, as we have seen, the somewhat divergent observations as well as would smoothed values made from these observations themselves. Intermediate values may be obtained by linear interpolation:

---

[1] As reduced by Dr Edgar Buckingham, whom we have to thank for a private communication on the subject. His value, 357.1°, was on the scale S b p. = 444.9°, and we have adjusted it to our scale

TABLE VII.—VAPOR PRESSURES OF MERCURY FOR EVERY TWO DEGREES.

Temp. thermodynamic, press. mm. Hg at 0° and normal g. Extrapolated values in italics.

Temp.	0°.	2°.	4°	6°.	8°.
0°	*0.000207*	*0.000252*	*0.000306*	*0.000370*	*0.000447*
10	*0.000537*	*0.000645*	*0.000773*	*0.000922*	*0.00110*
20	*0.00131*	*0.00155*	*0.00183*	*0.00216*	*0.00254*
30	*0.00299*	*0.00350*	*0.00410*	*0.00478*	*0.00558*
40	*0.00648*	*0.00752*	*0.00872*	*0.01008*	*0.01163*
50	*0.01340*	*0.01541*	*0.01768*	*0.02027*	*0.02319*
60	*0.02648*	*0.03020*	*0.03439*	*0.03909*	*0.04437*
70	*0.05029*	*0.05692*	*0.06432*	*0.07258*	*0.08179*
80	*0.09204*	*0.1034*	*0.1161*	*0.1301*	*0.1457*
90	*0.1628*	*0.1818*	*0.2028*	*0.2259*	*0.2513*
100	*0.2793*	*0.3100*	*0.3438*	*0.3807*	*0.4212*
110	*0.4655*	*0.5140*	*0.5668*	*0.6245*	*0.6873*
120	*0.7557*	*0.8301*	*0.9109*	*0.9987*	*1.094*
130	*1.197*	*1.309*	*1.430*	*1.560*	*1.701*
140	*1.854*	*2.018*	*2.195*	*2.385*	*2.59*[illegible]
150	*2.811*	*3.047*	*3.302*	*3.574*	*3.866*
160	*4.179*	*4.514*	*4.873*	*5.256*	*5.665*
170	*6.102*	*6.568*	*7.065*	*7.594*	*8.158*
180	*8.758*	*9.396*	*10.07*	*10.79*	*11.56*
190	*12.37*	*13.23*	*14.15*	*15.11*	*16.14*
200	*17.22*	*18.36*	*19.58*	*20.86*	*22.21*
210	*23.63*	*25.14*	*26.72*	*28.40*	*30.16*
220	*32.01*	*33.96*	*36.02*	*38.18*	*40.45*
230	*42.83*	*45.34*	*47.96*	*50.72*	*53.62*
240	*56.64*	*59.82*	*63.15*	*66.64*	*70.29*
250	*74.10*	*78.09*	82.27	86.63	91.19
260	95.94	100.91	106.09	111.50	117.14
270	123.02	129.14	135.52	142.17	149.09
280	156.29	163.78	171.57	179.66	188.08
290	196.81	205.92	215.31	225.14	235.31
300	245.85	256.79	268.13	279.89	292.07
310	304.69	317.77	331.30	345.32	359.82
320	374.82	390.34	406.39	422.97	440.13
330	457.85	476.20	495.06	514.59	534.74
340	555.54	576.99	599.13	621.97	645.57
350	669.77	694.78	720.56	747.11	774.45
360	802.62	831.60	861.44	892.15	923.75
370	956.25	989.68	1024.0	1059.4	1095.7
380	1133.0	1171.4	1210.7	1251.2	1292.8
390	1335.4	1379.2	1424.1	1470.2	1517.6
400	1566.1	1615.8	1666.9	1719.2	1772.9
410	1827.5	1884.1	1941.8	2000.9	2061.4
420	2123.4	2186.9	2251.9	2318.3	2386.4
430	2456.0	2527.3	2600.1	2674.7	2753.6
440	2828.8	2908.5	2990.0	3073.1	3158.2
450	3245.0	*3333.8*	*3424.5*	*3517.1*	*3611.7*

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

STUDIES IN VAPOR PRESSURE: V. A DYNAMIC METHOD FOR MEASURING VAPOR PRESSURES, WITH ITS APPLICATION TO BENZENE AND AMMONIUM CHLORIDE.

BY ALEXANDER SMITH AND ALAN W. C. MENZIES.

Received September 10, 1910.

For high vapor pressures, to the measurement of which a vessel closed with a rubber stopper is unsuitable, a modified form of the submerged bulblet apparatus[1] may be used. The new apparatus is less easily constructed, but, when made, has several advantages, for all purposes, over the simpler form. To avoid repetition, we mention only the few points in which the new apparatus differs from the old, and refer the reader for all further description and directions, and for a discussion of the theory and characteristics of the method, to the former papers. This instrument, to distinguish it from the static apparatus described in a preceding paper, will be called the "dynamic isoteniscope."

THE EXPERIMENTAL METHOD.

The Apparatus.—The opening *C* (Fig. 1) is connected with the gage, the exit to the air, and the pressure (or vacuum) bottle and pump.[2] The bulb *B* (diameter 23 mm.) contains the liquid through which the stream of vapor is discharged. The bulblet *A* is made as a separate part and, after being charged with the solid or liquid substance under investigation, is fused on to the side tube at the dotted line. When cut apart carefully at this point, after use, the apparatus may be employed repeatedly. The bulb between *A* and *B* prevents access of the liquid in *B* to the bulb *A*. The total length from *B* to *C* is about 30 cm.

The method of manipulation is the same as that described in connection with the submerged-bulblet vapor pressure apparatus.[3]

Necessary Corrections.—When the apparatus is employed, the usual precautions and corrections in connection with the gage and thermometer are required. Two corrections are peculiar to this apparatus. One is that for immersed depth, measured in this instance from the surface of the liquid in *B* down to the opening of, or the point of ascension in, the capillary.[4] The second is that due to capillary ascension, which increases the pressure beyond that shown by the gage.[5] The amounts of both corrections may be measured together as follows: After the observations are completed, and the bulb *A* has been cut off, the opening

---

[1] Submerged bulblet papers: THIS JOURNAL, 32, 897 and 907.

[2] For general arrangement, see this series, No. III, Fig. 3.

[3] *Loc. cit.*

[4] THIS JOURNAL, 32, 901.

[5] *Ibid.*, 32, 902.

C is connected with a wide tube standing in a beaker of water. The latter tube is raised, drawing its water content with it until the surface of the confining liquid in *B* falls to the point of ascension, or until bubbles issue from the capillary, as the case may require. The elevation of the water above the surface in the open beaker gives the value in water height of the capillary effect plus the submerged-depth effect. This is reduced to mercury height at 0°, and added to the gage pressure, as usual. The interior of the capillary must be wet with the substance just before the measurement is made. As we have seen, the amount of these corrections is small.

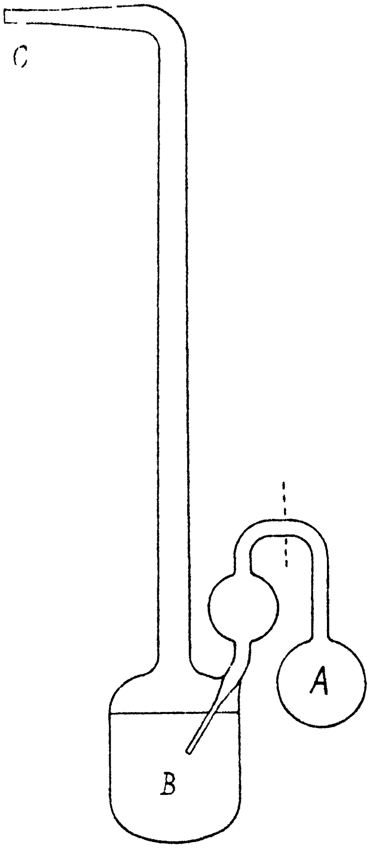


Fig. 1

Characteristics of this Method.—The valuable characteristics of the submerged-bulblet apparatus, which have already been described in full are, of course, retained in this dynamic isoteniscope. This form of the apparatus possesses, however, several additional advantages: (1) It can be used for high pressures as well as low. (2) The test tube in the former apparatus contains a large volume of the confining liquid. This acquires the temperature of the outside bath—and therefore transmits it to the bulb of the thermometer—rather slowly. Here the quantity of the confining liquid is much smaller. Then, too, the thermometer is hung directly in the bath liquid and a slight lag in the temperature of the confining liquid in the bulb *B*, if any existed, would have little or no effect upon the vapor pressure values obtained. This arrangement, therefore, permits the making of measurements of equal accuracy more rapidly. (3) The thermometer is not subjected to varying pressures, and the correction for the dilatation[1] of the bulb when the pressures are below 760 mm. is eliminated. Correction for compression of the bulb, due to the immersion in a liquid, may be made, but the magnitude of this correction is very small, averaging only 0.02° for 10 cm. immersion in water.

---

[1] THIS JOURNAL, 32, 905.

When compared with the static apparatus, this dynamic apparatus will be seen to retain all the characteristics enumerated when that apparatus was described,[1] and to possess several additional advantages: (1) There may be difficulty, with the static apparatus, in finding a suitable confining liquid. This difficulty cannot arise when the substance is a liquid, since the substance is employed in the U-tube to confine its own vapor. But when the substance is a solid, no liquid which has an appreciable vapor pressure of its own at the temperatures concerned, and none which interacts with the substance to give a gaseous product, and none in which the vapor of the substance is soluble, may be employed. Cases, such as those of the ammonium halides, phosphorus pentachloride, etc., therefore arise in which suitable confining fluids for certain ranges of temperature are hard to find. Thus, for ammonium chloride, fused silver chloride might be used, but would be available only above its melting point (450–460°). The present dynamic method is much more flexible, since possession of an appreciable vapor pressure by, or miscibility of the substance with, or chemical activity of the substance toward the confining liquid do not usually interfere with the operation of the apparatus, and would not, save in extreme cases, impair the accuracy of the results. The dynamic isoteniscope is therefore applicable to a wider range of cases.

(2) This dynamic method would find application when results by the static and the dynamic methods are to be compared. Such a case is mentioned, for example, by Smits and Scheffer,[2] who give reasons for anticipating that the values of the dissociation pressures of substances like aldehyde-ammonia might be widely different, according as the one or the other method was used.

This method has one disadvantage when compared with the static method, namely, that, in the latter, no corrections for submerged depth or for capillarity are required. The static method is therefore to be preferred, save where use of the dynamic one is indicated by considerations such as those mentioned in the preceding paragraphs.

The Sample Determinations.—As we have seen, water is at present the only substance suitable for testing the accuracy of a method of measing vapor pressures. The determinations with this substance, using the simple form of the submerged bulblet, have already shown, however, that an apparatus operating on this principle is capable of yielding results of a high order of accuracy. The present form of the apparatus was applied, therefore, to the measurement of the vapor pressures of benzene and of ammonium chloride.

The bath, stirrer, barometer, gage, and platinum resistance thermometer, and the corrections involved in their use, were the same as those employed in the work with the static isoteniscope.[1] It is sufficient here to say that the temperatures are on the thermodynamic scale, assuming the boiling point of sulphur to be 445°, and that the error below 120° (benzene) was ascertained to be less than ±0.01° and above 120° (ammonium chloride) less than ±0.1°.

---

[1] Studies in Vapor Pressure, III, Sec. 3, THIS JOURNAL, 32, 1419.

[2] *Z. physik. Chem.*, 65, 70 (1908).

THE VAPOR PRESSURES OF BENZENE.

Determinations by Previous Observers.—The sample used by Regnault[2] melted at 4.45°, nearly a degree too low, and must have been impure. He employed the dynamic method above 24°. Ramsay and Young[3] removed thiophene and otherwise purified their sample, but do not give the melting point. They used their dynamic method[4] (up to 80°), in which the liquid trickled onto cotton surrounding the bulb of the thermometer. In this instance they state that correction was made for the dilatation of the bulb of the latter *in vacuo*. Young[5] continued the series above 80° by the barometer-static method[6] over mercury, using a part of the original material, and giving temperatures on the scale of the constant-volume air thermometer. Neubeck[7] used purified benzene boiling at 79.9° at 760 mm. The freezing point is not given. He boiled the substance in a flask under reduced pressure. His thermometer was compared with an air thermometer, but he did not correct for dilatation of the bulb *in vacuo*. The values given below are obtained by graphic interpolation from his data. Mangold[8] used benzene from benzoic acid. He gives the melting point 5.5°. He used Schmidt's[9] dynamic apparatus and did not correct for dilatation of the thermometer bulb *in vacuo*. Kahlbaum[10] purified his benzene, but gives no melting point. He determined the boiling points under reduced pressure, admitting air through a capillary, and did not correct for dilatation of the thermometer bulb. Woringer[11] gives no melting point of his purified benzene. He used the static method, over mercury, admitting the substance through a stopcock, but gives no facts in regard to exclusion of dissolved gases. The results found by these six observers are tabulated along with our own below.

---

[1] *Loc cit.*

[2] *Mem. Acad.*, 26, 416 (1862).

[3] *Phil. Mag.*, [5] 23, 61 (1887).

[4] Criticized, this series, No. III, Sec. 2, THIS JOURNAL, 32, 1418.

[5] *J. Chem. Soc.*, 55, 486 (1889).

[6] Criticized, this series, No. III, Secs. 1 and 2, THIS JOURNAL, 32, 1414 and 1416

[7] *Z. physik. Chem.*, 1, 649 (1887).

[8] *Sitzungsber. Math.-Nat. Klasse, Kaiserl. Akad.*, 102 (IIa), 1071 (1893).

[9] *Z. physik. Chem.*, 7, 441.

[10] *Ibid.*, 26, 600 (1898).

[11] *Ibid.*, 34, 262 (1900).

Purification of the Benzene.—Kahlbaum's "thiophenfrei," crystallizable benzene was used. It was boiled under reflux with much sodium for three hours, at the end of which time no trace of hydrogen evolution could be detected. It was distilled, and the middle portion of the distillate, amounting to 1.46 liters, was used. This came over, after correction of the temperatures for changes in the barometric pressure, within 0.01°. A portion used for a freezing-point determination was boiled for fifteen minutes to remove dissolved gases. The freezing point was taken by two thermometers, the ice points of which had been ascertained immediately before, and they agreed in giving the value +5.40°.

The physical properties of benzene have been carefully investigated by Lackowitz,[1] who found that they were greatly affected by dissolved air. He showed, for example, that the removal of dissolved air, not considered by previous observers, produced a marked lowering in the specific gravity. His freezing point was 5.42 ± 0 02°. The lower freezing points of previous observers, namely, Regnault 4 45°, Jungfleisch 3 00°, W. Fischer 5.3, and Schoop 5.04, undoubtedly indicate insufficient purification. Linebarger[2] found 5 4° and Mangold 5 5°. Only Flink[3] claims to have reached 6.06°.

It appears, therefore, that our sample was probably as pure as that of Lackowitz. Even if we ignore the possibility, which he admits, that his freezing point may have been 0.02° too high, and assume that ours was lower than his by the same amount, the proportion of impurity which this represents would not noticeably affect the accuracy of the results. At the boiling point (about 80°) it would give an elevation of only 0 01° and lower the vapor pressure by only 0 2 mm. This is the maximum effect reached by assuming that the whole of the supposed impurity was involatil, for our method provides for the removal of dissolved gases during the measurement.

The Vapor Pressures of Benzene.—Concentrated sulphuric acid was used as confining liquid in the bulb *B*. Since benzene vapor is soluble in this liquid, the reading was taken when the liquid had ascended the capillary to a fixed mark. Correction was made for submerged depth and for capillarity. The values obtained were as follows:

T..	63 16	66.55	71 09	74 79	80.30	90.48	95.67	100.42	105.97	111.54	119 93
P..	439 1	492.0	563.7	640.8	765 5	1031	1197	1364	1581	1820	2235

The observed pressures were plotted against the temperatures, a smooth curve was drawn through the resulting points, and the value of the pressure every 5° was read off. The results are given in the following table: For comparison, the corresponding values of Regnault (Rg), Ramsay and Young and Young (Y), Neubeck (N), Mangold (M), Kahlbaum (K), and Woringer (W) are given. The essential details of their methods have been discussed already.

---

[1] *Berichte*, 21, 2210 (1888).

[2] *Am. Chem. J.*, 18, 437.

[3] *Beibl., Ann. Physik*, 8, 262.

t.	S & M.	Rg.	Y.	N.	M.	K.	W.
65°	463	463.4	...	465	468	..	...
70	551	547	548	550	554	546.5	559.5
75	650	643	...	645	653	...	...
80	757 5	752	755	760	764.5	750	773.5
85	879	..	.		...	..	...
90	1018	1013	1008	...	..	...	..
95	1180	...		...	...	...	...
100	1348	1340	1335	...	...	...	...
105	1542		.	...	...	...	...
110	1751	1744	1739	..	...	...	...
115	1983	....		...	...	...	...
120	2240	2235	2230	...	...	..	...

The boiling point, 80 12° at 760 mm., was also read from the curve. The values found by different observers are as follows:

Kopp (1847) .	80 40°	Ramsay and Young (1887) .	80 2°
Regnault (1863) .	80 36	Neubeck (1887) . .	79 9
Brühl (1880) . .	80 08	Louguinine . . .	80 20
Flink (1884) . . .	80 37	Smith and Menzies (1910)	80 12

THE VAPOR PRESSURES OF AMMONIUM CHLORIDE.

In order further to test the value of the dynamic isoteniscope method of measuring vapor pressures, we sought some substance difficult of study by the older methods. A non-fusing solid, the vapor of which attacked mercury, was required. That comparison might be possible, it was desirable also that the vapor pressures of the substance should have been previously determined by more than one observer and using methods professing some degree of accuracy. Ammonium chloride seemed to be the only such substance. Even with the present exceedingly adaptable method, this salt presented a problem of exceptional difficulty, and the results cannot claim the same degree of accuracy as do those with water and benzene. It will appear, however, that even in this case the limits of accuracy can be stated, and that the results are free from the undefined, and undoubtedly considerable sources of error with which the previous determinations may be charged.

Previous Determinations.—The vapor pressures of this salt have been determined by Horstmann,[1] by Ramsay and Young,[2] and by F. M. G. Johnson.[3] Horstmann's method was a dynamic one. He heated ammonium chloride in a combustion tube and noted the readings of a mercury thermometer immersed in the vapor, while the pressure of the air in the tube rose by stages from about 10 mm. to 760 mm.

---

[1] *Ber.*, **2**, 137 (1869).

[2] *Phil. Trans.*, **177**, 71 (1886).

[3] *Z. physik. Chem.*, **61**, 458 (1908); **65**, 36 (1908).

Ramsay and Young made a large number of observations by several methods. One series from 98° to 280° was obtained statically over mercury in a barometer tube. Some permanent gas accumulated during the observations, and the value at the highest of these temperatures, for example, may be in doubt on this account alone about 0.5° (or 4.5 mm. = 3 per cent. of the whole). Observations from 290° to 340° were secured by enclosing a lump of the salt above a constriction in the closed limb of a U-tube. The bend was filled with mercury, and air pressures of known value could be applied to the vapor of the metal through the open limb. The U-tube was heated by the vapor of mercury boiling under various known pressures, and the corresponding temperatures were taken from Regnault's data, with an error, therefore, of 1° at 340°. Foreign gases and vapors were expelled by lowering the pressure, and allowing the vapor of the salt to escape past the mercury in the U-tube. At 320° and 340° the vapor pressure of the ammonium chloride did not give a constant value, but increased continuously. At 320° this increase was a linear function of the time, but the rate of increase per minute varied in different experiments from 0.2 mm. to 1 mm. per minute. The increase was under observation for as long as 390 minutes in one instance. With the help of time curves, the observations were corrected. This increase is attributed by the authors to the liberation of hydrogen by chemical action of the hydrogen chloride on the mercury. At 340° there was always a very rapid rise in pressure, amounting to from 32 to 67 mm., during the first twenty minutes, before the slower, uniform rise (of from 0.2 to 1 mm. per minute) set in. The authors suggest that the salt was cooled by the immediately preceding, rapid vaporization, and during the twenty minutes was regaining the temperature of the vapor bath. But this effect should have been almost as great at 320°, where no rapid rise was observed. In explaining both of these increases in pressure, the authors ignore entirely the effect of diffusion of the mercury vapor backwards to the surface of the salt. The result of this diffusion must be to increase the pressure and, if complete interdiffusion of the vapors had occurred, the limit would have been reached only when the total pressure equaled the sum of the vapor pressures of ammonium chloride and mercury. The evident fact is that when the confining liquid has a considerable vapor pressure of its own, and the interdiffusion of the vapors is possible during the observation, the resulting measurements of vapor pressure must always be of uncertain value. When we consider the fact that here the vapor pressure of the confining liquid, although less than that of the substance, was of the same order (at 320°, the pressures are 369 mm. and 445 mm., and at 340°, 548 mm. and 760 mm., respectively), it is surprising that the readings could be utilized at all.

The same observers made an independent series of measurements by their dynamic method, described in an earlier paper.[1] Here a block of the salt surrounded the thermometer bulb, and the distilling vessel containing the thermometer was heated by means of boiling mercury. The observations were made from 178.5° to 338.9°. The results, when plotted, were found to be somewhat scattered, and all on one side of the rather smooth curve that could be drawn through the points determind by the static method. The pressures at corresponding temperatures are all higher, being at 320° on an average about 56 mm. higher (estimated graphically), at 330° about 80 mm. higher, and at 333.5° about 100 mm. higher. The results by the static and dynamic methods, separately, as well as the values finally adopted, are given in a table at the close of this paper. A supplementary observation by a different dynamic method, in which the mass of the salt surrounding the thermometer bulb was placed in a combustion tube and heated with a Bunsen burner, gave a value at 338.35° of 762.1 mm. This confirmed the results by the static method rather than those by the dynamic, being less than 2° (equivalent to about 35 mm.) below the static temperature at the same pressure, while the dynamic temperature at the same pressure was 6° below static. Hence, the dynamic results were considered to be the less trustworthy, and in the curve which embodies the final results, much greater weight is given the static results. The final data are therefore essentially derived from a static method. The authors state that the difference of less than 2° above mentioned "may well be due to error of experiment." The results at the highest temperature are thus estimated to be subject to an error of at least ±2°, or, according to their curve, ±35 mm. Considering the extreme experimental difficulties involved in the method, this error cannot be considered excessive. The specific sources of error in these methods have already been discussed at length.[2]

F. M. G. Johnson employed the Ladenburg manometer, consisting of a flattened glass tube, wound in a spiral. The external pressure required to bring the attached mirror back to the zero position was measured. His method was therefore static, but he avoided the great difficulties connected with the common static methods in which mercury is used. Assuming that, as the author says, the spiral was capable easily of showing a pressure change of "the order of 1 mm." (although he does not state that this degree of sensitiveness was maintained at 335°), the chief errors to which his method was liable arise from four causes, namely, gases ocoluded in or absorbed by the solid substance, unequal distribution of temperature in the air bath he used for heating, the untrustworthiness of mercury thermometers at such high temperatures, and the unfortunate method used for standardizing the thermometers. The efficiency of the whole arrangement was, indeed, tested by a determination of the vapor pressures of iodine, and the results were found to agree well with those of Ramsay and Young. But the test ranged from 80.5° to only 178.5°, while the experiments with ammonium chloride ran from 211° to 335°. The temperature errors would not assert themselves strongly until above 200°, so that this test cannot be accepted as a rigid demonstration of the adequacy of the precautions. Attention must therefore be drawn to the sources of error individually.

---

[1] *Phil. Trans.*, 175, 37 (1886); *J. Chem. Soc.*, 47, 42 (1885).

[2] This series, No. III, Secs. 1 and 2, THIS JOURNAL, 32, 1413–9.

The apparatus and material were freed thoroughly from moisture by means of phosphorus pentoxide, and to effect this the former was pumped out repeatedly and left evacuated for a long period. The apparatus was heated during the process, for the purpose of assisting the desiccation and of driving out adhering air. But the parts containing the pentoxide and the salt could not be heated. The salt had previously been sublimed twice. It will be seen, however, that the complete expulsion of adhering gases was not insured. The quartz spiral gage used by Preuner and Schupp[1] is so constructed as to permit of boiling out before sealing, when vapor pressures are to be determined. But this process could not be applied when, as was the case with Johnson's apparatus, a bulb for the simultaneous determination of the vapor density was attached. It is a pity that the zero of the gage was not redetermind after the experiments, as this would not only have shown whether any permanent gas had been liberated, but would also have afforded a means of detecting other irregularities, such as a permanent distortion of the spiral.

Johnson's apparatus was heated in an unstirred air bath provided with a gas pressure regulator which kept the temperature constant ± 1°. As we have seen,[2] however, an air bath is by far the least satisfactory means of keeping the temperature uniform and constant. Aside from the inherent causes of defective thermal equilibrium, in this case a copper tube was inserted through the top of the bath, forming a separate compartment surrounding the pocket containing the solid ammonium chloride. The purpose of this was to keep the salt cooler than the bulb and spiral. The temperatures in the copper tube and in the rest of the bath differed by 22° at 323°. Now, if maintaining *one* temperature in an air bath is difficult, keeping *two* temperatures each constant and uniform is much more difficult. This feature of the apparatus, therefore, involves a source of considerable uncertainty.

The temperatures were ascertained with a nitrogen-filled, mercury thermometer. It is well known, however, that such a thermometer, when kept for a considerable time at a high temperature, suffers distillation of the mercury into the upper part of the bore,[1] and gives untrustworthy readings, with an error of about ±1°. On account of the difficulty in making due correction, the error is greater when the thread is not completely immersed.

---

[1] *Z. physik. Chem.*, 68, 129.

[2] This series, No. III, Sec. 1, THIS JOURNAL, 32, 1413.

Finally Johnson standardized the thermometer by using the vapor pressure curve of mercury. The data used were those of Ramsay and Young.[2] Young,[3] however, has himself pointed out and corrected some of the most serious inaccuracies which have meantime come to light in these data. His corrections alter the temperature at 340° by 1°.

The present status of our knowledge of the vapor pressures of ammonium chloride may now be summed up. Horstmann makes no professions of exact thermometry and ±5° at the highest temperature is a conservative estimate of the limits of error involved. The known error of Ramsay and Young's measurements is ±1° at the lower temperatures and ±2° at the highest. But the uncertainty of interpreting the progressive increase in the pressures at 320° and 340° introduces an additional possibility of error, the magnitude of which cannot be assessed. Johnson's measurements are affected by such considerable temperature errors, the most serious of which are of unknown magnitude, that his measurements can be regarded as approximate only. In considering all these determinations, it must be remembered that, at 335°, an error of ±1° corresponds to an error of ±15 mm. in pressure. It is therefore evident that the vapor pressures of ammonium chloride are in need of re-determination by a method which permits of the definite estimation of the limits of error involved.

The Vapor Pressures of Ammonium Chloride.—The bulb *A* (outside diameter 22 mm.) was filled completely with ammonium chloride. The latter, Kahlbaum's purest form of the salt, was finely pulverized and was purposely used without drying. Since the method itself involves a fractionation, special treatment to remove volatil impurities was unnecesssary. Hydrochlorides of coal-tar bases were proved to be absent.

The bath was filled with the mixture of potassium and sodium nitrates, and, no other transparent, fusible substance of a suitable nature being available, the outer bulb *B* was charged with the same mixture. The ammonium chloride vapor, in passing through this liquid, caused a continuous production of nitrous oxide. The method was therefore seen under the greatest disadvantage, since it was impossible to observe a complete cessation of the stream of vapor. The pressure taken was that at which the stream of gas reached a minimum volume.

---

[1] Ostwald-Luther, *Physikochem Mess*, [1902] 78. In such a thermometer we have frequently observed with a lens droplets of mercury and particles of a red substance (HgO?) accumulating above the thread.

[2] *J. Chem. Soc.*, 49, 37 (1886). We are indebted to the author for privately informing us of this fact.

[3] *J. Chem. Soc.*, 59, 629 (1891).

Our temperature error of less than ±0.1° corresponds at the lowest temperature to ±0.25 mm. and at the highest to ±1.5 mm. These are therefore the limits of error of the apparatus *per se.* The difficulty in observing the point of minimum gas evolution, however, introduces a special source of error peculiar to this substance. From a consideration of the degree of sharpness with which the observations could be made, we estimate this error at about ±5 mm. in the individual readings. The consistency of our results, as shown by the way in which they lie upon a smooth pressure-temperature curve, confirms our belief that the errors are not greater than this.

The following results are corrected for immersed depth and for capillarity, and are given to the nearest millimeter:

Temperature........	278.3	291.6	298.7	308.5	316.4	325.4	332.9
Pressure............	131	199	240	322	406	518	633

For comparison, the data of Horstmann (two points, ×), Ramsay and Young[1] (curve I), Johnson, undried substance[2] (curve II), and Smith and Menzies (curve III), are plotted in Fig. 2. It will be seen that the last curve lies between the other two.

The following table contains the data read from the various curves. As throwing some light on the relative trustworthiness of Ramsay and Young's static and dynamic methods, as applied to a substance like this, the observations obtained by each of these have been treated separately and the resulting pressure readings are given in two additional columns:

		R & Y.				
			Observations.			
t.	H.	Curve.	Static.	Dynamic.	J.	S & M.
280	...	143	140.5	147	132	138
290	...	195.5	189	200	178	189
300	259.5	264.5	251	275	237	252
310	...	350	333.5	367	309	336
320	...	460.5	443.5	500	401	447
330	...	599.5	596	675	518	587
333.5	...	661	653	750	566	642
340	778.1	777	759.5	...	678	...

From this comparison it will be seen that Ramsay and Young's static results, when taken by themselves, agrees remarkably well with our dynamic results, the divergencies exceeding the estimated error of our measurements, namely ±5 mm., only above 320°. The inferiority of their

---

[1] Reproduction of the author's own curve. Johnson ignores the curve, which embodies the authors' conclusions from all their observations, and uses for comparison only certain of the single observations, all taken from the static series.

[2] Dr. Johnson informs us that in his first paper (p. 462), the last temperature, 335°, should be 345°. In the curve on the opposite page, the 211° point is misplaced. In the second paper (p. 37), the NH_4Cl curve is incorrect.

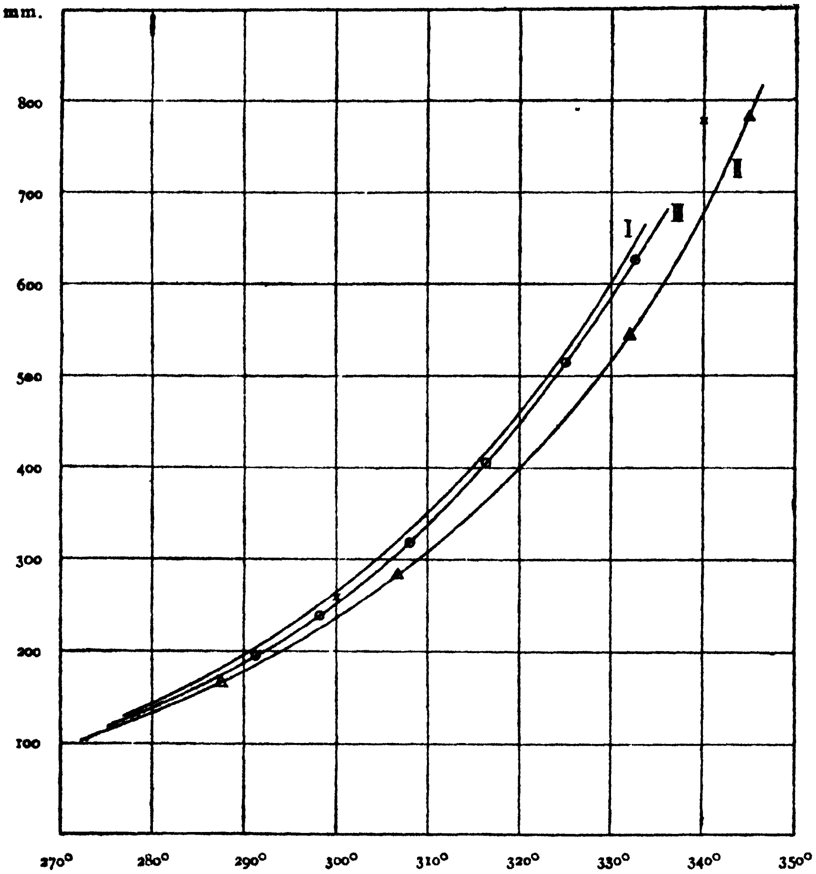


Fig. 2.

dynamic method, at least when applied to a substance like this, is apparent.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 61.]

THE POTENTIAL OF THE SODIUM ELECTRODE.

BY GILBERT N. LEWIS AND CHARLES A. KRAUS.

Received October 3, 1910.

The electrode potentials of a number of important groups of metals have not been measured hitherto, because their action upon water is such as to preclude the possibility of obtaining equilibrium conditions. Among these groups, those comprising the alkali metals and the metals of the alkaline earths are the most notable examples. In the present paper we shall describe a method which may be employed in the determination of electrode potentials of this kind. We shall show, moreover, that this method permits the determination of the potential of the sodium electrode with a higher degree of precision than has yet been reached in the case of any other solid electrode.

Our problem, consisting in the determination of the potential of metallic sodium against an aqueous solution of sodium ion of normal concentration, can evidently be solved only by indirect means. We have found it possible with certain precautions to measure the potential of a dilute sodium amalgam directly against an aqueous solution. It only remained, therefore, to find the difference between this potential and that of pure sodium. This difference in potential measured in any cell where the only process which accompanies the current is a transfer of sodium from the pure state to the dilute amalgam, must be independent of the nature of the electrolyte used. We succeeded in measuring this difference in potential in a cell containing sodium and sodium amalgam electrodes, and an electrolyte composed of a solution of sodium iodide in liquid ethyl amine.

The Electrode Potential of Dilute Sodium Amalgam.

The dilute sodium amalgam used throughout this investigation was prepared and preserved in the apparatus shown in Fig. 1. A bulb, E, is connected by means of a small capillary, F (having a uniform bore of about 0.2 mm.), with a straight tube, GK. While this tube is open at K, a piece of metallic sodium (Kahlbaum) is cut from a larger piece, quickly rolled into cylindrical form and placed in the tube at G. A small glass rod, H, is placed immediately above to serve as a weight in the operation about to be described. The tube is then sealed at K and the apparatus exhausted at A through the 3-way cock B, the cock J being closed and the cock I open. When the apparatus is completely exhausted I is closed and J, which communicated with a reservoir of ammonia (not shown in the figure), is opened for an instant, thus filling the tube IJ with pure ammonia gas. The tubes F and G, and the lower part of E are now surrounded by a paraffin bath and heated gradually to the melting point of sodium. When this point is reached, and the liquid sodium, pressed by the glass weight above, breaks its thin shell of oxide, the cock I is opened cautiously and the pressure of the ammonia slowly forces the molten sodium into the bulb E. The sodium is thus filtered by the small capillary from every trace of oxide or other solid impurity and appears as a bright metallic globule. The paraffin bath is now removed and the capillary is sealed off at F, the left-hand portion of the apparatus being thus removed. After the exhaustion has been continued to remove all of the ammonia gas, pure mercury is allowed to enter the bulb D at C (from an apparatus not shown in the figure) and the tube C is sealed off. B is closed. The lower part of the apparatus, comprising the bulbs E and D and the connecting tube, is then warmed in a paraffin bath to 180° centigrade. The mercury vapor passing slowly from D to E amalgamates quietly with the sodium. When the latter is completely amalgamated, the apparatus is allowed to cool. It is then shaken to provide for thorough mixing of the contents and clamped in an inverted position. It may now be sealed at A to any apparatus in which the sodium amalgam is desired and the filling carried out *in vacuo*. The 3-way cock B merely serves to facilitate the cleaning of the tube A after such a filling.

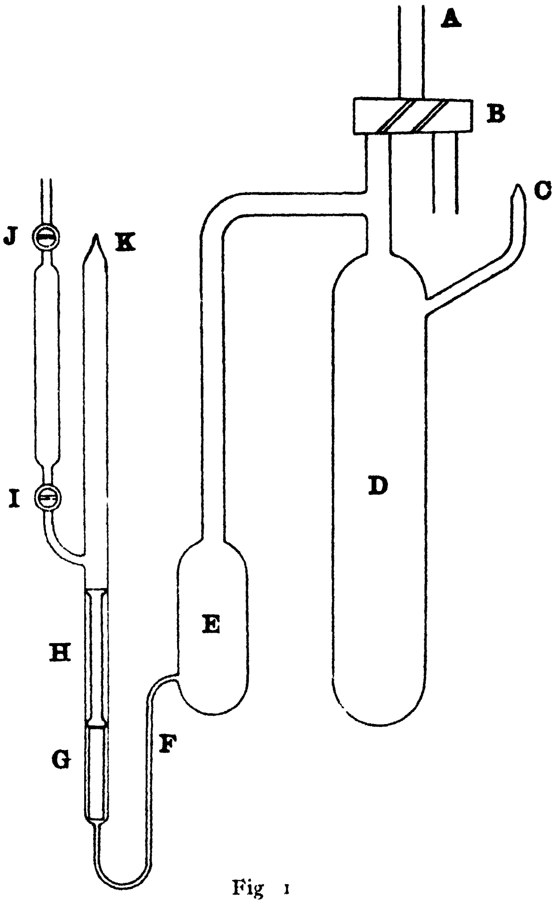


Fig 1

The amalgam so prepared and kept does not differ in appearance from pure mercury, and remains unchanged for years.

Two portions of the sodium amalgam were treated with standard hydrochloric acid until the sodium was removed, and the remaining acid was titrated with standard alkali. According to these two analyses (which agree within less than 0.1 per cent.) 100 grams of amalgam contained 0.2062 gram of sodium.

In determining the potential of this amalgam against fifth normal sodium hydroxide, a portion of the amalgam was introduced into the reservoir sketched in Fig. 2. This reservoir was sealed to the apparatus of Fig. 1 (at the points Q and A) and after complete exhaustion the amalgam was allowed to enter through the cock B. The reservoir was then sealed at Q. The side tube L contained phosphorus pentoxide and per-melted the entrance of dry air to take the place of amalgam drawn off through M. The amalgam surface at P formed the electrode and electrical contact was provided through a platinum wire sealed in at N. The tube OP was inserted in a half-cell of the usual type, filled with 0.2 *N* NaOH, and was joined thereto by a rubber stopper, O. This half-cell dipped into another containing 0.2 *N* NaCl, which in turn communicated with 0.2 *N* KCl and finally with a normal calomel electrode. The whole system was placed in a thermostat at 25°.

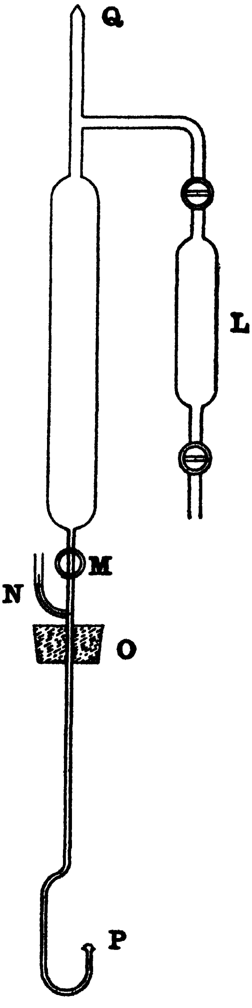


Fig. 2.

The amalgam surface at P when first placed in the sodium hydroxide evolved considerable hydrogen. The action appeared to take place at certain spots where a few extremely minute solid particles accumulated. The extraordinary influence of small amounts of catalyzers in this action of sodium amalgam upon water has already been pointed out.[1] Fortunately it was found that by opening the cock M and allowing one or two drops of amalgam to flow out at P, the minute particles that seemed responsible for the action were carried down. The new surface was acted upon less vigorously, and after this process had been repeated a number of times the surface remained clear of hydrogen for ten to twenty minutes, and showed a constant and perfectly reproducible potential within 0.1 millivolt.

The measured electromotive force was then 2.1749 volts,[2] inclusive of liquid potentials, for the combination, Na amalgam (0.206 per cent.); NaOH 0.2 *N*; NaCl 0.2 *N*; KCl 0.2 *N*; KCl *N*; normal electrode (N. E.).

The liquid potential between KCl *N* and KCl 0.2 *N* is negligible. That between NaOH 0.2 *N* and NaCl 0.2 *N* is 0.0287 v.; that between NaCl 0.2 *N* and KCl 0.2 *N* is 0.0050 v.[3]. Both these potentials oppose the main

---

[1] Walker and Patterson, *Trans. Am. Electrochem. Soc.*, 3, 185 (1903); Lewis and Jackson, *Proc. Am. Acad.*, 41, 403 (1906).

[2] This experiment was repeated with the same amalgam nearly two years later and gave the electromotive force 2.1742 volts. Considering the possible change in the composition of the amalgam and the use of different electrical standards, this may be regarded as a satisfactory check.

[3] Lewis and Sargent, This Journal, 31, 363 (1909).

e. m. f. of the cell. Adding these figures, therefore, to the measured e. m. f. we obtain for the above cell, exclusive of liquid potentials,

Na amalg. (0.206 per cent.), NaOH 0.2 *N*, N. E.; E. = 2.1986 v.

In order to calculate now the potential of this amalgam against sodium ion at normal concentration, it is necessary to know the degree of dissociation of fifth normal sodium hydroxide. Instead of calculating this directly from conductivities, we shall assume provisionally, for reasons that will be explained in another place, that the degree of dissociation of 0.2 *N* NaOH is the same as that of 0.2 *N* KCl, and that the latter is 82.8 per cent., as found from conductivities. If now we apply the Nernst equation, we find

Na amalg. (0.206 per cent.), Na^+N, NaOH 0.2 *N*, Na amalg. (0.206 per cent.); E = 0.0461 v.

Combining this equation with that given above we find

Na amalg. (0.206 per cent.), Na^+N, N. E.; E = 2.1525 v.

The Difference in Electrode Potential between Sodium and Dilute Sodium Amalgam.

The difference in electrode potential between sodium and a sodium amalgam in the same electrolyte will be independent of the nature of that electrolyte, provided it is one in which the metal and the amalgam act as completely reversible electrodes. Our problem consisted, therefore, in finding a solvent which is not attacked by sodium, and which dissolves some sodium salt to form a conducting solution. Ethyl amine was finally chosen as the solvent, and attempts were made first to use sodium chloride and sodium bromide as solutes, but neither of these substances proved to be sufficiently soluble to give the solution the desired conductivity. Sodium iodide, however, proved to be extremely soluble and its solution is an excellent conductor.

Anhydrous ethyl amine was prepared and kept for use in the following way. About 200 cc. of Kahlbaum's ethyl amine were treated for several days with metallic lithium, the solubility of which in the amine makes it especially efficient in removing water and other objectionable impurities. The liquid was then distilled into a vessel shown in Fig. 3.

The volatility of ethyl amine, and its great solvent power for such substances as are commonly used for stopcock lubricants, prevents its storage in an apparatus closed with ordinary stopcocks. For this reason a special form of valve, shown in Fig. 3, was designed. The ethyl amine is stored in tube A. In the position of the apparatus shown in the figure, its vapor may pass freely out through B, C, and the cock D. The lower part of the valve HGF contains mercury. The glass plunger I is rigidly connected with an iron rod, J, encased in a sealed glass tube. By means of a magnetic helix placed around J, this plunger may be raised or lowered. If lowered it causes the mercury on the right-hand side to rise and lift a glass float, E, which is ground to fit the conical end of the tube C. The mercury rises above this joint, tightly sealing the exit tube C. If the cock G is now closed the helix may be removed and the apparatus remains sealed until it is desired to withdraw more amine from the reservoir, when the plunger is once more raised and the valve opened. The cock D prevents the entrance of air into the reservoir when the vapor pressure of the amine falls below atmospheric pressure.

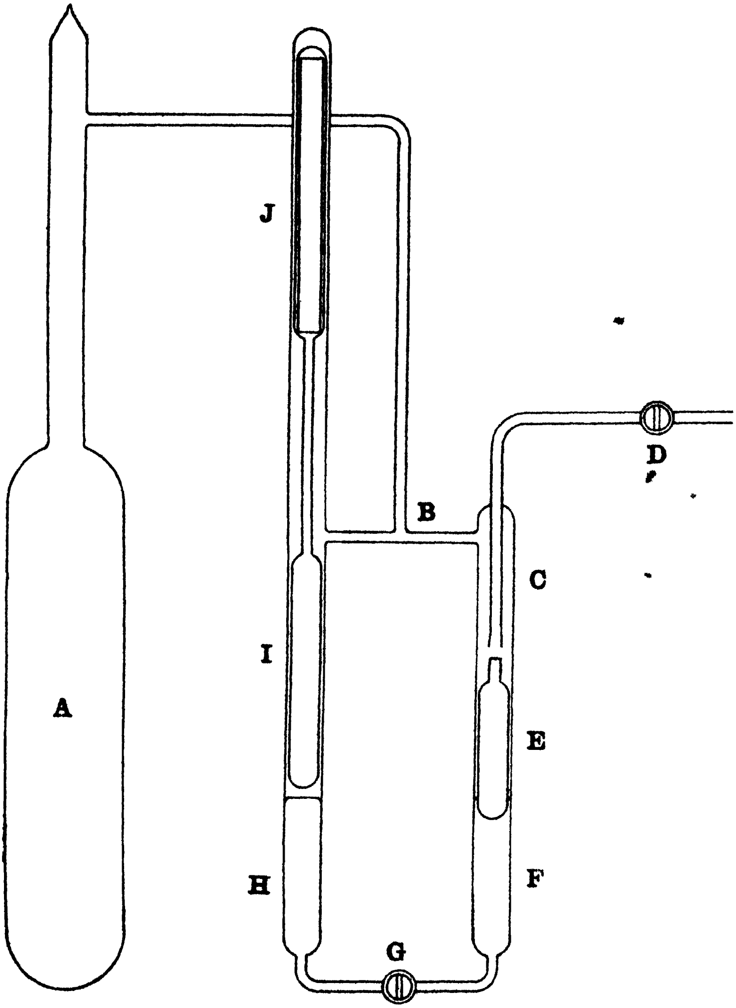


Fig. 3.

The cell in which the measurements were made is shown in Fig. 4. Two platinum wires are led to the electrodes through the tubes K and L. The capillary P is connected with the device for introducing metallic sodium, which we have already described. The tube Q is sealed to the ethyl amine reservoir, the tube S to a vacuum pump, and the tube N to the amalgam reservoir. A suitable amount of dry sodium iodide is introduced through the tube M which is then sealed off. The apparatus is thoroughly exhausted, sodium is introduced at P by the method already described, and the tube P is sealed off. The apparatus is further exhausted, the amalgam is allowed to enter through the tube N which is then sealed off. The connection to the pump is then sealed off at S. Finally the cell is cooled in ice, and the valve of the amine reservoir being opened, the amine is allowed to distil in until it rises above the connecting tube R. The tube Q being now sealed off, the cell is entirely free and its contents may be thoroughly stirred by slowly tipping from one side to the other. The bulge in the cell at O prevents any amalgam from reaching the sodium electrode in this process. The platinum terminals are completely covered, one by amalgam and the other by metallic sodium.

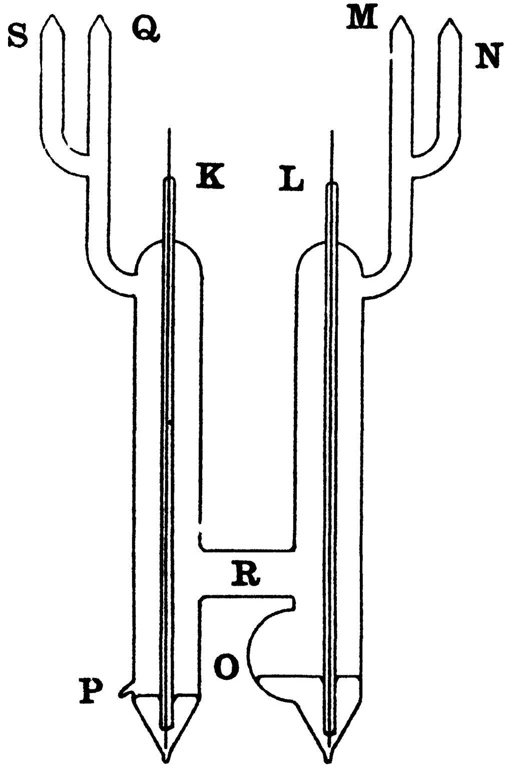


Fig. 4

In the first cell that was set up, the sodium surface became coated with a substance that we assumed to be sodium hydroxide. The cell gave, however, a very constant electromotive force of 0.8457 v. at 25°. The coating we attributed to the presence of a trace of water in the sodium iodide, which, though it had been heated and dried, was in the form of powder and might have taken up some water while being introduced. The cell was therefore refilled, using sodium iodide which had previously been fused. This time the sodium surface was perfectly clean and remained so after the cell had stood many days.[1]

This cell gave immediately after its preparation a constant electromotive force which did not change during a number of days, in which measurements were made. Differences of 0.1 to 0.2 millivolt occasionally were found but disappeared when the contents of the cell were stirred. The electromotive force at 25° was 0.8456 v., which is only 0.1 millivolt different from that found above in the cell with the coated sodium surface. Another cell filled in the same way, containing a relatively small amount of sodium iodide, also gave 0.8456 v. A good idea of the constancy of the cell may be obtained from the following measurements made to determine the temperature coefficient of the electromotive force. The cell was changed back and forth from a thermostat at 10° to one at 35°. The electromotive force at 10° was about 1 millivolt higher than at 35°, the successive differences measured being 0.00100, 0.00093, 0.00091, 0.00100, 0.00101, 0.00102, 0.00103, 0.00103, 0.00102, the last six differences were constant within 0.00003 volt and we may take $0.00102 \div 25 = 0.0000408$ as the diminution in electromotive force per degree rise of temperature. It is evident that the cell exhibits a higher degree of constancy and reproducibility than any cell having an electrode of solid metal which has hitherto been studied. The electromotive force of such cells usually varies very greatly, owing to surface changes in the metal. It was perhaps to be predicted that in the case of so soft a metal as sodium, such variations would not appear.

The Potential of the Sodium Electrode; the Heat of Solution of Sodium in Mercury.

In order to determine finally the electrode potential of sodium against a normal solution of sodium ion, it is only necessary to add the difference between the potentials of sodium and sodium amalgam to the electrode potential of the amalgam obtained above. This gives

$$\text{Na, Na}^{+}N\text{, N. E.; E} = 0.8456 + 2.1525 = 2.9981 \text{ v.}$$

On account of some slight uncertainty as to the electrical standards used, this final value of the potential of sodium may be in error by nearly 1 millivolt.

Wilsmore[2] in his valuable critique on electrode potentials calculated the potentials of some of the metals which decompose water from the heats of formation of their salts, according to Thomson's rule. He calculated for the sodium electrode the potential of 3.10 v. against the calomel electrode, a value differing from ours by 102 millivolts.

---

[1] In the course of a few weeks a very thin black coating appeared on the metal surface and after two years' standing a considerable portion of the sodium has disappeared.

[2] *Z. physik. Chem.*, 35, 291 (1901).

The temperature coefficient of the cell with sodium and sodium amalgam electrodes permits a remarkably accurate calculation of the heat of solution of sodium in a 0.206 per cent. sodium amalgam. We may use the equation of Helmholtz

$$E - \frac{Q}{F} = T\frac{dE}{dT},$$

where Q is the heat evolved in the solution of one equivalent of sodium in a very large quantity of 0.206 per cent. amalgam. F is the Faraday equivalent, 96580 coulombs. Substituting 0.8456 for E, and —0.0000408 for dE/dT, we find $Q = 82850$ joules or, if one calorie is equal to 4.186 joules, $Q = 19790$ calories. Were it not for some uncertainty as to the exact value of the factor to be used in passing from volts to calories, the above value of Q would be reliable within 2 or 3 calories. Berthelot found by calorimetric methods the heat of solution of sodium to form a 0.5 per cent. amalgam equal to 18800 calories. The difference between this value and ours is probably to be attributed to the heat of dilution of the amalgam from 0.5 to 0.2 per cent.

The method of handling an amalgam of an oxidizable metal, which we have described, may be of use in other lines of investigation than the present one, especially in the determination of the electromotive force of amalgam concentration cells. For this purpose the amalgams might be compared with one another in aqueous solutions by means of the apparatus of Fig. 2, but in many cases it will be preferable to work in amine solutions where the oxidation of the amalgam may be completely avoided. It is not, however, our intention to prosecute this line of research, but rather to investigate in the immediate future the electrode potential of other metals of the alkalies and alkaline earths by the method which we have found so successful in determining the potential of sodium.

In conclusion, we wish to express our indebtedness to the Bache fund of the National Academy for a grant which enabled us to carry out this investigation.

Summary.

The potential of sodium in a normal solution of sodium ion at 25° is found to be 2.9981 volts against the normal calomel electrode taken as 0.

This is the sum of two values (1) 2.1525 volts, the potential of 0.206 per cent. sodium amalgam against normal sodium ion and (2) 0.8456 volts, the difference in potential between sodium and 0.206 per cent. sodium amalgam, in a solution of sodium iodide in ethyl amine.

The temperature coefficient of the latter electromotive force is —0.0000408 volt per degree. Hence, from the Helmholtz equation, the heat evolved when one equivalent of sodium dissolves in a large quantity of 0.206 per cent. sodium amalgam is 19790 calories.

Methods are described for preparing and keeping pure sodium amalgam and anhydrous ethyl amine, and of measuring the true potential of the amalgam of an oxidizable metal in aqueous solution.

BOSTON, MASS., June 24, 1910.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ELECTROLYTIC DETERMINATION OF CHLORINE IN HYDROCHLORIC ACID WITH THE USE OF A SILVER ANODE AND A MERCURY CATHODE.

BY JACOB S. GOLDBAUM AND EDGAR F SMITH

Received July 23, 1910.

With the introduction of the silver anode and mercury cathode, many new and interesting determinations and separations have been effected. Much attention has been paid in this laboratory to this phase of electroanalysis, and exact and satisfactory results have been obtained.[1]

Recently there appeared an article by Gooch and Read[2] on the "Electrolytic Determination of Chlorine in Hydrochloric Acid, with the Use of the Silver Anode." From this communication it would seem that upon extending the analysis of chlorides, in neutral aqueous solution, to the determination of chlorine in free hydrochloric acid, the method as presented in previous communications from this Laboratory yields values which are "very irregular and always low." It is, therefore, proper to consider the question raised by Gooch and Read, and to submit additional evidence, together with some of the details of procedure.

Experiments were made with hydrochloric acid precisely as described by Gooch and Read, and behaviors similar to those noted by these chemists were observed; that is, the electrolysis resulted, not only in the fixation of chlorine at the anode and the liberation of hydrogen at the cathode, but also in a secondary decomposition, which gave rise to the production of hypochlorites. As a consequence, some of the silver of the anode dissolved in the electrolyte, and at times appeared at the cathode. The fixation of the oxygen at the anode was likewise observed and, indeed, when this oxygen was driven off, low and non-concordant results were obtained. Now, in these experiments a platinum cathode was employed and with the exception of a single determination, the experiments performed by Gooch and Read were with a platinum cathode, whereas, in all the work done in this laboratory on the fixation of anions, a mercury cathode has been employed. Indeed, Gooch and Read were really not using "similar means," and the criticism of the original method because of the failure of an altered arrangement is hardly fair. Hence, it is only natural that we should try the effect of a silver anode and mercury cathode in the analysis of hydrochloric acid, and to this end, experiments were accordingly conducted.

---

[1] THIS JOURNAL, 29, 447, 1445, 1455, 1460; *Ibid.*, 30, 1706.

[2] *Am. J. Sci.*, 544 (1909).

The platinum gauze anode was plated with silver from a potassium silver cyanide electrolyte. It is true, as stated in the article by Gooch and Read, that there is a possibility of the retention of some soluble cyanide in the gauze, even after the plated anode has been treated with boiled water, and subsequently ignited gently. We have been aware of this fact, however, for several years, and while making no mention of it, have succeeded in obviating the difficulty by dipping the freshly plated silver gauze in dilute hydrochloric acid, washing it thoroughly with distilled water, and then igniting it to incipient redness in a low Bunsen flame. By this means, any admixed cyanide is destroyed. The solution undergoing analysis could not then become contaminated by material derived from the plating bath. Care should be taken not to ignite the anode too strongly in the Bunsen flame, as it is most desirable that the silver should not fuse, and that its porous nature should be preserved. A complete retention of the chlorine is favored by these means, whereas with a smooth silver surface there is a possibility that molecular chlorine may be liberated, with a consequent production of hypochlorites and chlorates.

Another fact, known to us for some time, is the secondary formation of oxide upon the anode along with the halide. To obviate its disturbing effect upon the weight of the anode, we have had recourse to a home-made electric oven heated to 300°. Silver oxide is completely decomposed at 250°, giving off oxygen and leaving metallic silver, so that at the end of an electrolysis the anode is at once placed in an oven with the temperature mentioned for a period of ten or fifteen minutes, when nothing will remain but silver and silver chloride, so that the increase in weight of the anode would represent only the weight of the added halogen. These and certain other perfections of our original procedure in the analysis of halides in the double cup, which have come as results of experience, will be more fully described in a later communication relating to the determination of the atomic weight of chlorine in the electrolytic way.

During analysis, the anode should not be placed too near the cathode. By observing this point a too-high current density will be avoided and one need not fear a possible loss due to the loosely adherent silver halide because of its too-rapid formation. It is advisable with the pressure usually employed (2.5–5 v.) with the double cup to place the anode at least 15 mm. from the level of the mercury. No turbidity of the electrolyte will then follow.

The hydrochloric acid used in the determinations which appear in this paper was standardized by the well-known precipitation method with silver nitrate. The residue from 40 cc. of the solution, containing

0.1418 gram of hydrogen chloride, weighed 0.0001 gram. Only freshly distilled water was used for dilution. In the first two determinations, a "double-cup" was used, but since in the case of hydrochloric acid this presented no advantage over a cell with a single compartment, the latter was employed for the subsequent determinations. This cell consisted of an ordinary beaker, 6 cm. in diameter and 8 cm. high, containing a layer of pure mercury 3 mm. deep. Cathode connection was made with the mercury by means of a platinum wire sealed in a glass tube. The anode was the usual disk gauze type. It made 300 revolutions per minute. The total dilution of the electrolyte was 90 cc. The liquid remaining in the beaker after the current was interrupted was found in every case to be neutral to methyl orange, and when tested with silver nitrate and with starch, and potassium iodide, hypochlorous acid or hypochlorites were invariably absent. In experiments 3 and 4 the electrolyte showed a slight turbidity, due to the fact that the electrodes were too close. In all other determinations the liquid remaining after the electrolysis was perfectly transparent and clear. The liquid from determinations 8 and 9 was evaporated to dryness and gave no appreciable residue. The mercury used for cathode had been distilled several times and was carefully examined for silver before and after the electrolysis, but none was found. Hence there was no transference of the metal from the anode to the cathode.

	Chlorine taken in HCl, gram.	Time. Min.	V.	A	Chlorine found.	Error.
1	0.0709	20	2.5–5.0	0.85–0.01	0.0707	—0.0002
2	0.0709	22	2.5–5.0	0.80–0.005	0.0710	+0.0001
3	0.1418	28	2.5–5.0	0.95–0.01	0.1410	- 0.0008
4	0.1418	30	2.5–5.0	0.95–0 015	0.1406	—0.0012
5	0.0709	20	2.5–5.0	0.85–0.005	0.0703	—0.0006
6	0.1418	30	2.5–5.0	0.80–0.005	0.1418	+0.0000
7	0.1418	35	2.5–5.0	0.75–0.005	0.1416	—0.0002
8	0.0709	20	2.5–5.0	0.75–0.005	0.0709	±0.0000
9	0.0709	20	2.5–5.0	0.80–0.005	0.0707	—0.0002
10	0.0709	23	2.5–5.0	0.65–0.01	0.0710	+0.0001
11	0.1418	35	2.5–5.0	0.80–0.005	0.1420	+0.0002

From the foregoing tests it would appear that the electrolytic determination of chlorine in hydrochloric acid by means of a silver anode and mercury cathode is not only possible but is, moreover, extremely accurate and reliable.

Since the preceding determinations were made, W. B. Coleman, a student in this laboratory, carried out a series of determinations of bromine in hydrobromic acid. The results obtained by him are submitted in the following table. These results confirm those obtained with chlorine and prove beyond question that this method of analysis is reliable and exact.

HYDROBROMIC ACID

Br present in gram.	V.	A N.D.$_{80}$.	Time. Min.	Br found in gram.	Remarks.
0.0700	4	0.4 –0.01	35	0.0685	Solution turbid after electrol.
0.0700	4	0.4 –0.02	35	0.0683	Solution turbid after electrol.
0.0700	3	0.35–0.01	35	0.0698	Clear solution.
0.0700	3	0.35–0.002	50	0.0699	" "
0.0700	3	0.35–0.002	50	0.0697	" "
0.0700	3	0.35–0.003	50	0.0698	" "
0.0700	3	0.35–0.003	50	0.0696	" "
0.0700	3	0.35–0.001	50	0.0700	" "
0.0700	3	0.35–0.001	50	0.0696	" "

UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

ELECTROLYTIC SEPARATIONS.

BY IRVING H BUCKMINSTER AND EDGAR F. SMITH

Received July 23, 1910.

During the last three years there have been carried out in this laboratory certain metal separations in the electrolytic way, which may be of interest to those who are engaged in work of this character, so that it seems only proper that the results should be brought together in a single communication. The following paragraphs give in sufficient detail all the data necessary for those who may have occasion to repeat the separations. Thus, the separation of mercury from nickel was conducted in the presence of sulphuric acid. The anode consisted of a flat platinum spiral, which was rotated. The cathode was an ordinary platinum dish. With 0.1437 g. of mercury, and 0.2772 g. of nickel in the presence of 0.1 cc. of concentrated sulphuric acid, a current of N. D.$_{100}$ = 0.3 amp. and a pressure of 2.9 volts there was precipitated in the course of thirty-five minutes 0.1436 gram of mercury. Again, 0.2876 g. of mercury was separated from 0.1386 g. of nickel in the presence of 0.1 cc. of concentrated sulphuric acid, by the means of a current of N. D.$_{100}$ = 0.3 amp. and a voltage of 2.8 in a period of forty minutes. Six additional separations with conditions like those just indicated resulted similarly, so that we may regard this as a satisfactory procedure for the separation of mercury from nickel. The deposits of mercury were in every instance examined for nickel, but it was not found.

In the separation of bismuth from nickel 0.2772 g. of nickel and 0.2640 g. of bismuth, in the presence of 1 cc. of concentrated sulphuric acid, were exposed to the action of a current of N. D.$_{100}$ = 0.3 amp. and 2.2 volts for forty-five minutes. The deposit of bismuth weighed 0.2642 g. It was free from nickel. Six additional experiments resulted similarly. The deposits of bismuth, however, were not coherent, and the greatest care was required in washing them to avoid loss of the metal.

In separating copper from nickel, the metals were present as nitrates and there was added 1 cc. of nitric acid, specific gravity 1.4, while a current of N. D. $_{100}$ = 0.3 amp. and 2.4 volts was allowed to act upon 0.1481 g. of copper and 0.2772 g. of nickel. There was completely precipitated in forty minutes 0.1482 g. of copper. In the five additional experiments, conducted under practically the same conditions, the results were equally good, and the separation may, therefore, be considered successful. The deposit of copper was perfectly adherent and bright in color. At no time was nickel found in the copper.

In endeavoring to effect a separation in nitric acid of silver from nickel in practically the same manner as just described under copper from nickel, the silver deposits were not very adherent, but upon adding 5 cc. of ordinary alcohol to the electrolyte, containing 0.2191 g. of silver and 0.1386 g. of nickel, in the presence of 0.3 cc. of nitric acid, specific gravity 1.4, a current of N.D.$_{100}$ = 0.1 amp. and 1.1 volts, precipitated in 45 minutes 0.2192 g. of silver. Eight additional trials were conducted and with results that were very satisfactory. In the absence of alcohol, there was invariably a considerable anodic deposition.

Another interesting separation was that of mercury from nickel in a nitric acid electrolyte. The results which were observed in a number of experiments are represented in the single one which is here offered: 0.2477 g. of mercury as nitrate and 0.1386 g. of nickel as sulphate, in the presence of 3 cc. of nitric acid of specific gravity 1.4, were electrolyzed with a current of N. D.$_{100}$ = 0.3 amp. and 1 volt. In 30 minutes 0.2476 g. of mercury was precipitated. The deposits of mercury were, in all instances, bright and metallic, and in no case was the metal found contaminated with nickel.

Three trials leading to the separation of lead from nickel in nitric acid were carried out without the slightest difficulty. Lead was, of course, precipitated as dioxide upon a sand-blasted dish. In this instance the rotating cathode consisted of a perforated dish. The variation in the quantities of lead found ranged from 0.0001 to 0.0003 g.

From the many separations of zinc from nickel which were carried out in the presence of an alkaline tartrate electrolyte, one may be given. With a current of N. D.$_{100}$ = 0.3 amp. and 2.4 volts, in the presence of 1 g. of Rochelle salt and caustic potash sufficient to precipitate and redissolve the hydroxides, 0.1430 g. of zinc and 0.1386 g. of nickel as sulphates were acted upon for a period of 45 minutes. 0.1433 g. of zinc was found.

In an electrolyte containing free phosphoric acid, the separation of copper from nickel is quite satisfactory. In the same electrolyte, an attempt to separate cadmium from nickel was unsuccessful. The cadmium was deposited very slowly, and almost invariably contained nickel. The separation of mercury from nickel in a phosphoric acid electrolyte is also quite good.

In attempting to separate nickel from aluminium in the well-known ammonia and ammonium sulphate electrolyte, aluminium hydroxide invariably attached itself to the nickel deposit and was not fully removed by water. However, upon adding a little dilute sodium hydroxide the aluminium hydroxide at once disappeared, and the nickel was then washed with pure water. Proceeding in this way, three experiments gave most satisfactory results Upon attempting to separate nickel from iron in a similar electrolyte, it was discovered that the ferric hydroxide was apt to contaminate the deposit of nickel. In this electrolyte nickel may be successfully separated from magnesium and the alkaline earth metals, although, of course, in the case of the latter, some other ammonium salt than the sulphate should be used. Indeed, in separating nickel from barium, as well as from strontium and calcium, the electrolyte was introduced into a small beaker, a gauze cathode being bent so that there was a clearance of about 5 mm. between it and the anode, and about the same distance between it and the beaker. The weight of the anode was 15 g. and the cathodes were about 5 g. each. By this contrivance, the separations, ten in all, were conducted very satisfactorily, and with results that were extremely concordant.

In attempting to separate nickel from chromium in the presence of ammonium hydroxide and ammonium sulphate no deposit was observed after two hours, although a current of 0.8 of an ampere with a pressure of 2.5 volts was employed. At first chromium hydroxide, of course, separated and was soon oxidized. This peculiar retention of the nickel led to trials with cobalt in a similar electrolyte. Indeed, it was soon discovered that in an ammonium hydroxide and ammonium sulphate electrolyte containing cobalt, an electrolyte which under ordinary circumstances answers splendidly for cobalt as it does for nickel, upon the addition of potassium chromate there was absolutely no deposition of metallic cobalt. This did not take place even after several hours' passage of the current; and strangely enough, when the electrolyte was removed from the platinum dish its pink color suggested the presence of cobaltammine. When hydrochloric acid was added to the solution, and the latter warmed gently, quite an abundance of purpureocobaltic chloride separated out. As this happened in a number of trials, it was concluded to make this method of preparing a cobaltammine the subject of a special study, which is now in progress and the results of which will be reported in a later communication. Upon the addition of potassium chromate to an ammonium hydroxide and ammonium sulphate electrolyte containing copper, the deposition of metallic copper was also completely prevented. This curious behavior led us to add the same reagent, potassium chromate, to a solution of silver nitrate containing ammonium hydroxide and ammonium sulphate. Upon the passage of a current of 0.6 of an ampere with a pressure of 2.5 volts, the silver was precipitated in an adherent and weighable form upon the cathode. This difference in behavior of silver and copper in an electrolyte, such as has just been described, led to an attempt to separate these two metals. The five experiments instituted resulted most satisfactorily. The deposits of silver were perfectly coherent and light gray in color and were readily washed. This separation, however, would not be used in place of other older and just as reliable methods.

A problem of considerable interest to electro-analysts has been the separation of silver from gold. A reference to early papers communicated from this laboratory will show that on several occasions a marked difference of deportment in various electrolytes justified the hope that this separation had been realized. Upon testing out the new methods, however, they were found to be inadequate. The remarkable behavior of the metals copper, silver, nickel and cobalt when exposed to the action of the current in the presence of potassium chromate led Mr. J. T. Lay, of this laboratory, to let the current act upon a solution of gold chloride, containing ammonium sulphate and ammonium hydroxide, with a considerable quantity of potassium chromate. To our amazement, gold was not precipitated, although the current was increased to 3 amperes with a pressure of 5.6 volts.

Again, the thought came that now a separation of silver from gold in this new electrolyte might be obtained. While fairly good separations were reached, it was impossible to remove the last traces of silver without carrying down some gold, so that our hopes were cast to the ground. When for a moment one considers the new electrolyte, and the peculiar behavior of the metals, it seems altogether likely that complexes of the most varied nature must exist in the electrolyte.

A few attempts were made with the copper salt in the presence of ammonium hydroxide, ammonium sulphate and potassium chromate to determine the electromotive force of the combination, with the result that very few free copper ions were found, all of which would indicate that in such a solution there are probably complexes, the exact nature of which it is not possible for us at the present moment to give. These are receiving proper consideration.

The determination of zinc in a potassium cyanide electrolyte has been discussed at various times, and there has always been a difference of opinion as to the conditions under which success could be obtained. Our experience has shown that if to a zinc salt solution there be added sufficient caustic potash to completely precipitate the zinc as hydroxide, with enough of cyanide to just redissolve the precipitate, in the presence of 20 cc. of ammonium hydroxide of specific gravity 0.96, a current of 2 amperes with a pressure of 5 volts will precipitate 0.1487 gram of zinc in from 15 to 30 minutes. Six successful experiments confirmed this result. The deposition of the zinc was made upon a silver-coated platinum dish. The total dilution did not exceed 100 cc. With these conditions, substituting nickel and cobalt for zinc, there was no deposition of either metal, so that it was hoped that by observing the preceding conditions it might be possible to separate zinc from nickel and cobalt in such an electrolyte. All of the results proved the contrary. It is a well-known fact that lead and manganese, when deposited from solutions containing nitric acid by the current, appear in the form of peroxides at the anode. If, however, the volume of nitric acid be increased to from 15 to 30 cc. acid, specific gravity 1.46, it was found that with quantities of metal like the following, namely 0.0982 gram of lead and 0.0555 gram of manganese, and a current of 8.5 amperes with a pressure of 4.5 volts, in 20 minutes there was deposited 0.0980 gram and 0.0979 gram of lead. Eight experiments of this character were made. The deposits of lead dioxide were all that could be desired. Upon testing, however, each of these eight deposits, traces of manganese were found. Perhaps these were due to occlusion. The deposits were made upon a dish anode and the cathode made to revolve 250 times per minute. It should be added that even with twice the quantity of lead given in the preceding paragraph, the separation was apparently as exact as with the small amount, but traces of manganese were found in this larger quantity of lead.

The metal bismuth may be deposited in a perfectly adherent form, and, at the same time, separated from tungsten and from molybdenum, if conditions similar to those shown in the following examples be observed: 0.1926 gram of bismuth as nitrate, 0.1862 gram of tungsten as sodium tungstate, 3 grams of tartaric acid, 0.5 of a gram of sodium hydroxide, and a current of 0.2 ampere with a pressure of 3 volts. The anode was rotated and the bismuth was precipitated upon the platinum cathode. Its quantity was 0.1928 gram. The time of precipitation did not exceed 30 minutes. The quantity of molybdenum used in a number of successful trials was 0.1 of a gram.

A separation that has generally been regarded as difficult in the electrolytic way is that of silver from bismuth. In our study of this problem more than eighty-three determinations were made. We submit two results, showing the conditions which proved most favorable: *Experiment 1.*—To a solution containing 0.0637 gram of silver as nitrate and 0.0875 gram of bismuth as nitrate was added 0.15 of a gram of ferric alum and 0.15 of a gram of chrome alum. The dilution of the electrolyte was 100 cc. Upon adding 6 cc. of nitric acid, specific gravity 1.47, and electrolyzing with a current of 0.15 of an ampere and a pressure of 1.3

volts, there was precipitated in 30 minutes 0.0634 gram of silver. *Experiment 2.*—To a solution containing 0.1274 gram of silver as nitrate and 0.0875 gram of bismuth were added 0.1 of a gram of ferric alum and 0.2 of a gram of chrome alum. The solution was again diluted to 100 cc., and after the addition of 7 cc. of nitric acid of specific gravity 1.4, a current of 0.15 of an ampere and pressure of 1.3 volts precipitated in forty minutes 0.1274 gram of silver. It was noticed that when the pressure exceeded 1.5 volts, some bismuth peroxide appeared at the anode, and that traces of metallic bismuth were found in the silver deposit. It was noticed, also, that alum alone was not sufficient to retain the bismuth in solution. The temperature of the electrolyte varied from 25° to 30°.

Since these experiments were made, Dr. W. N. Chapin, of this laboratory, has repeated the work, with the following satisfactory results:

Silver.	Bismuth. Gram.	Ferric alum. Gram.	Chrome alum. Gram.	HNO_3. cc.	Volts.	Amperes.	Temperature. Degrees.	Time. Min.	Silver weighed.	Tests
0.0994	0.1	0.09	0.2	3	1.3	0.15	30	105	0.0990	No Bis
0.0994	0.1	0.09	0.2	3	1.3	0.15	30	105	0.0990	" "
0.0994	0.1	0.09	0.2	3	1.3	0.15	30	75	0.0996	" "
0.0994	0.1	0.09	0.2	3	1.3	0.15	30	70	0.0996	" "
0.0994	0.1	0.09	0.2	3	1.3	0.15	30	90	0.0992	" "

He has also found that the separation may be effected without the introduction of either of the alums. The conditions which he discovered to be wholly satisfactory were these: Silver 0.1 to 0.2 of a gram, bismuth 0.1 to 0.2 of a gram, 3 cc. of nitric acid in a total volume of 75 cc., temperature 60°, pressure 3 volts and current N. $D._{100}$ = 0.15 to 0.20 ampere. A dish anode was employed and placed 3 mm. from the dish cathode. The anode made 250 revolutions per minute. It is expedient to maintain the voltage constant and allow the electrolysis to proceed until the amperage falls to 0.002. By observing these conditions Dr. Chapin succeeded in making the separation in 25 minutes. The deposit of silver was perfectly free from bismuth. The electrolyte contained no silver.

Since mercury and silver are deposited under very similar conditions, it seemed probable that the preceding method would serve in the separation of mercury from bismuth. The experiments performed by Dr. Chapin prove this to be correct. The conditions observed by him were these: Total volume of electrolyte 75 cc., to which were added 10 drops of nitric acid. The pressure was 1.3 volts, the temperature of the electrolyte 50°. The dish anode was employed and rotated at the rate of 250 revolutions per minute. The current was allowed to fall to 0.002 amperes, using 0.1206 gram of mercury. The amounts obtained in two experiments with the above conditions were 0.1206 gram and 0.1208 gram. The amounts of bismuth were respectively 0.1000 and 0.2000 gram. Nitric acid exceeding the amount indicated above tends to prevent the last traces of mercury from separating.

Reference to the literature upon the separation of uranium in the electrolytic way from such metals as zinc, nickel and cobalt will disclose the fact that when using a platinum cathode with rotating anode, the uranium will be fully precipitated, but there seems to be a tendency on the part of the other metals to become enclosed in the deposit of uranium hydroxide. With this knowledge before us, it was thought worth the while to ascertain whether by employing a mercury cathode, the separations could not be made satisfactory. To this end there were made up stock solutions of zinc sulphate and uranium sulphate. Portions of these, representing 0.2071 gram of zinc and 0.1352 gram of uranium, were introduced into the mercury cup. 0.5 cc. of concentrated sulphuric acid was added, and with a current of 3.5 amperes and a pressure of 5 volts, zinc was completely precipitated in periods of time varying from 15 minutes to 60 minutes. The anode made 200 revolutions per minute. Twelve determinations were carried out with perfect success in every instance.

Cobalt and nickel sulphates were used in similar separations of these metals from uranium. The conditions were in the case of cobalt: 0.2036 gram of cobalt and 0.0322 gram of uranium, with 0.5 cc. of concentrated sulphuric acid, dilution 20 cc., current 5.6 amperes, pressure 7 volts, time 35 minutes; anode rotating 200 times per minute. The cobalt precipitated weighed 0.2034 gram. Eight determinations were made. In the case of nickel, the following conditions prevailed: 0.4290 gram of nickel and 0.0664 gram of uranium, with 0.5 cc. of concentrated sulphuric acid, and a current of 1.6 amperes, with a pressure of 5 volts. The anode performed 250 revolutions per minute. In 60 minutes there was precipitated 0 4288 gram of nickel. Eleven experiments confirmed the results of the preceding trial.

UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

SOME DERIVATIVES OF 2-ACETYL-NAPHTHOL-1.[1]

BY HENRY A. TORREY AND E. J. CARDARELLI.

Received August 27, 1910.

The 2-acetylnaphthol-1 used in this work was prepared and converted into its 4-nitro and 4-amino derivatives according to the method of Friedländer.[2] The free base, which had an orange-red color similar to that observed by him, was treated with thioacetic acid, when the monoacetyl compound obtained melted at 212°, whereas Friedländer's acetyl derivative (of which he gives no analysis) melted at 107°. He, however, used acetic anhydride in preparing his compound, and to make sure that our higher melting point was not due to our use of thioacetic acid we repeated the experiment with acetic anhydride and again obtained the monoacetyl compound melting at 212°. It is strange that we should have obtained a different result from Friedländer, as in at least one of our preparations we did our best to follow his directions. It is probable, however, that the difference was due to some change in conditions so trifling that we overlooked it. We regret that the pressure of other work prevented us from giving more time to this interesting subject.

---

[1] This research was suggested by the late Professor H. A. Torrey, and the greater part of the work was done under his direction, but the remainder of the work and the writing of the paper were deprived of the advantage of his supervision by his untimely death. C. L. JACKSON.

[2] *Ber.*, 28, 1946 (1895).

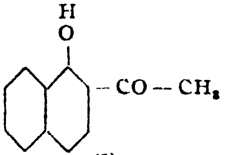
Two attempts to obtain a quinoline from the 2-acetylnaphthol-1 by the method of Skraup led to unpromising results. Accordingly, we turned our attention to the method of Döbner,[1] but upon heating our amine with benzaldehyde and pyruvic acid we obtained little or no quinoline, although we tried the experiment under a number of different conditions. We are of the opinion that the process would work if tried on a large scale, but the preparation of the amine is so troublesome that such experiments did not seem worth while. The difficulty in applying Döbner's quinoline synthesis to 2-acetyl-4-aminonaphthol-1 is the more striking, because it gives essentially quantitative results with other amines. The most obvious explanation for the inertness of this amine is to be found in steric hindrance, as the acetyl group stands in the ortho position to the atom of hydrogen which should have taken part in the synthesis. It was found in the course of these experiments that the amine acts with benzaldehyde in the cold, giving 2-acetyl-4-benzylidinamino-naphthol-1, $C_6H_5CHNC_{10}H_5(OH)COCH_3$, melting at 159°. The corresponding piperonylidine compound, melting at 178°, and that containing cinnamylidine, melting at 144°, were also made without difficulty. The yields are so good that perhaps this reaction might be developed into a method for the quantitative determination of aldehydes.

In the hope of reaching a quinoline more easily, the condensation of 2-acetylnaphthol-1 with orthonitrobenzaldehyde was undertaken, for the product by reduction and elimination of water might form a quinoline but experiments with this compound and with the meta- and paranitrobenzaldehyde showed that the reaction took place with such great difficulty that it was decided to work out the method with the cheaper meta compound before attempting to prepare the desired ortho derivative. The results of the numerous experiments tried under this head were far from inviting. The metanitrobenzaldehyde reacted with the 2-acetylnaphthol-1 with great difficulty; in fact it could not be made to act at all with most catalytic agents, potassium hydroxide in alcoholic solution being the only one found effective. With this the red 2-metanitrobenzalacetylnaphthol-1, $C_6H_4NO_2CHCHCOC_{10}H_6OH$, melting at 210°, was obtained, but in such small yields that it was not worth while to extend the research to the ortho compound. We can give no explanation of the fact that the nitrobenzaldehydes react with 2-acetylnaphthol-1 with so much more difficulty than the unsubstituted benzaldehyde.

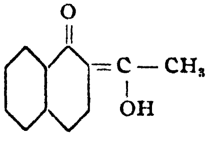
---

[1] *Ann.*, 249, 98, 110 (1888).

During the work on the action of benzaldehydes on the 2-acetylnaphthol-1 it was noticed that this latter substance was never recovered from the experiments in the form in which it had been introduced. Instead of crystallizing in very long, pale yellowish-green needles, melting at 103°, the recovered substance crystallized in brown plates melting constantly at 98°, so that at first we thought we had a new compound. We venture to suggest that the brown form may have a quinoid structure II, while the form melting at 103° is probably the phenol, I:



(I)



(II)

This view is in harmony with the observation of v. Kostanecki,[1] that in condensing benzaldehyde and acetonaphthol with 50 per cent. sodium hydroxide it was not necessary to add an acid, as the sodium salt was decomposed merely by dilution with water. The sodium salt of a substance with a structure like II would certainly act in this way, whereas it seems impossible that the salt of a true naphthol like I could be decomposed so easily.

By condensing benzaldehyde with 2-acetyl-4-nitronaphthol-1 the 2-benzalacetyl-4-nitro-naphthol-1, $C_6H_5CHCHCOC_{10}H_5NO_2OH$, was made, which melts at 203-208°, and resembles its isomer, $C_6H_4NO_2CHCHCOC_{10}H_6OH$, very closely, since that melts at 210°. In fact, the only marked difference is in the color—the first being orange-yellow, the second red. It is worth noting that the nitro group attached to the benzene in the red compound is nearer the double bond than that attached to the naphthalene ring in the orange-yellow substance. 2-Benzalacetylnaphthol-1 gave with nitric acid a nitro compound, which probably contained the nitro group on the naphthalene, to judge from its orange-yellow color and the melting point 206–208°, but it is obviously impossible to decide this point with certainty, owing to the strong resemblance between the two isomers.

As the orthonitrobenzaldehyde could be obtained only with difficulty, or at considerable expense, we next searched for some more accessible orthonitroaldehyde to replace it, and such a one was found in the 6-nitro-

[1] *Ber.*, 31, 705 (1898).

piperonal.[1] This substance had the further advantage of reacting easily even in the cold with the 2-acetylnaphthol-1, when sodium hydroxide was used as a catalyzer. The result, however, was not the condensation product expected, but the ketol, formed by direct addition of the aldehyde to the methyl of the ketone, the reaction being similar to the formation of aldol, $(CH_2O_2)NO_2C_6H_2CHO + CH_3COC_{10}H_6OH = (CH_2O_2)NO_2C_6H_2CH(OH)CH_2COC_{10}H_6OH$. An intermediate addition compound like this has been frequently assumed in considering the reactions between aldehydes and the methyl of a ketone, but, so far as we can find, none has been isolated as yet in the benzene or naphthalene series, for, if we have not overlooked some of them, only two are known, one made by the action of acetaldehyde and the other by the action of chloral on acetone. This is therefore the most important observation made in this research; and it is the more remarkable that the reaction should stop at the ketol, since with the other aldehydes that have been tried the unsaturated condensation product is formed with great ease, usually even in the cold.

This ketol may be called 2-(6-nitropiperonylalcohol)acetylnaphthol-1 or 1-(naphthol-1)-1-keto-3-hydroxy-3-(6-nitro-3,4-methylenedihydroxyphenyl)-propane. Its ketol structure is confirmed by the observation that one molecule of water is removed from it by acetic anhydride, or better, zinc chloride, leaving a substance melting at 226°; which will be described presently. Our work on the acetates is also in harmony with the ketol formula, although the end of the year cut it short, before we had removed the last doubt in regard to the nature of the diacetate. Fortunately, however, the ketol formula is firmly established without the aid of this additional confirmation. Acetic anhydride alone gave with the ketol a monoacetate melting at 188–190° (in addition to the compound melting at 226°), but, if sodium acetate was also present, what is probably a diacetate melting at 197–198° was formed. The ketol melts at 201–202°, so that the melting points of these three substances lie suspiciously near together, but their properties in other respects are so unlike that there can be no doubt they are different substances. As they contain percentages of carbon, hydrogen and nitrogen, showing differences hardly greater than the experimental errors of the analysis, it is impossible to settle their composition by analysis alone. It was proved, however, that the substance melting at 188–190° is the monoacetate by the analysis of its tribromo derivative, which would leave the formula of the diacetate for the compound melting at 197–198°, if it were not for the possibility that it may be a quinoid form of the monoacetate of the ketol. This view receives some confirmation from the fact that it crystallizes in rectangular plates, thus resembling the supposed quinoid form of 2-acetylnaphthol-1 discussed earlier in this paper;

---

[1] Fittig and Remsen, *Ann.*, 159, 134 (1871).

but it melts higher than the other form, whereas in that case the supposed quinoid melted lower; and the analysis agrees better with a diacetate than a monoacetate formula. These facts have led us to assign the formula of the diacetate provisionally to the substance melting at 197–198°, until its composition can be definitly fixed by additional experimental work, and we are the more ready to do this, because the quinoid form in the case cited rests at present only on a theoretical basis.

The substance melting at 226°, formed by treatment of the ketol with acetic anhydride or zinc chloride, differs from it by containing one less molecule of water, which might be split out in two different ways, forming either 2-(6-nitropiperonalacetyl)-naphthol-1, $C_6H_2(CH_2O_2)NO_2CH = CHCOC_{10}H_6OH$, or (6-nitro-3,4-methylenedihydroxyphenyl)-naphthoflavanone, $C_6H_2(CH_2O_2)NO_2\overbrace{CHCH_2COC_{10}H_6}^{O}$. The action of bromine on this substance gives a monobromo derivative formed with evolution of hydrobromic acid, and therefore pronounces in favor of the naphthoflavanone formula in spite of the fact that our substance is red, and all the flavanones, of which we can find accounts, are white, as it seems impossible that the dibromo addition product formed, if it were the piperonalacetyl compound, could be unstable enough to drop to the monobromo derivative spontaneously.

Experimental Part.

Acet-2-acetyl-4-aminonaphthol-1.—The 2-acetyl-naphthol-1 used in this work was prepared by the method of Friedländer[1] except that we found the boiling could be diminished from twenty to ten minutes, and a crystallization from glacial acetic acid removed most of the blue impurity thus facilitating the subsequent purification with alcohol. The nitro derivative also made by Friedlander's method was reduced with tin and equal parts of strong hydrochloric acid and water, added directly to the mixture of the ketone and the tin. Since the hydrochloride of the amino compound went into solution, as it was formed, it was easy to tell when the reduction was complete. The solution was filtered hot and the hydrochloride crystallizes on cooling in slightly yellowish needles, of which a small additional quantity was obtained by adding strong hydrochloric acid to the filtrate. On the addition of acid sodium carbonate to the aqueous solution of the hydrochloride the free base was obtained, of an orange-red color.

To convert this colored base into the acetyl compound, it was treated with thioacetic acid in molecular proportions, when a vigorous action at once set in, accompanied by evolution of hydrogen sulphide. The slightly yellow product, after crystallization from dilute alcohol, showed the constant melting point, 212°. As Friedländer obtained his acetyl com-

[1] *Ber.*, 28, 1946 (1895).

pound, melting at 107°, by the action of acetic anhydride, another portion of the 2-acetyl-4-aminonaphthol-1 was warmed gently with an excess of acetic anhydride. The product was diluted, allowed to stand, neutralized with acid sodium carbonate, and the precipitate, after crystallization from alcohol, also melted at 212°.

The analysis gave 5.86 per cent. N; calculated, 5.76 per cent.

It is therefore a monoacetyl compound, as the diacetyl derivative would give N 4.91. Whether the acetyl group is attached to oxygen or nitrogen must be left undecided in the present state of our knowledge.

Properties.—It crystallizes from dilute alcohol in microscopic needles, arranged like chestnut burs, and has a yellowish white color, which we think belongs to the compound, as it could not be removed by crystallization, even when assisted by boneblack. It melts at 212° and is soluble in alcohol, chloroform, or benzene.

2-Acetyl-4-benzylidenaminonaphthol-1, $C_6H_5CHNC_{10}H_5(OH)COCH_3$.—This substance was obtained in an attempt to convert the 2-acetyl-4-aminonaphthol-1 into a quinoline. As two experiments with Skraup's method had yielded unpromising results, we tried the method of Döbner,[1] and for this purpose made a mixture of the ketone, benzaldehyde and pyruvic acid in absolute alcohol; crystals were deposited almost immediately, which, after purification, showed the constant melting point 159°. Pyruvic acid with the ketone in absolute alcohol gave no action in 30 minutes, and even after an hour only a very small amount of a green powder had been deposited from the solution, which had turned red. On the other hand, when a solution of the ketone in absolute alcohol was mixed with benzaldehyde, crystals separated almost at once. After purification these melted as before, at 159°. The yield was 95% of the theoretical.

The analysis gave 4.89 per cent. N; calculated for $C_{19}H_{15}O_4N$, 4.84 per cent.

Properties.—The benzylidene compound forms small, lustrous plates between the colors of brass and bronze. Melting point 159°. Slightly soluble in cold, soluble in hot alcohol; soluble in ether, chloroform, tetrachloride of carbon, acetone, ethyl acetate, or benzene. Ferric chloride decomposes it, forming as one of the products benzaldehyde, which was recognized by its smell.

2-Acetyl-4-piperonylidenaminonaphthol, $C_6H_3(O_2CH_2)CHNC_{10}H_5(OH)$-$COCH_3$.—This substance was obtained in almost quantitative yield by allowing solutions of the free base and piperonal in absolute alcohol to stand for fifteen minutes. It could also be obtained from the hydrochloride and piperonal, but in this case the alcoholic solution needed heating for thirty minutes, and the product was much less pure. After crystallization from alcohol it showed the constant melting point 178°.

---

[1] *Loc. cit.*

Calculated for $C_{20}H_{15}O_4N$, N: 4.20. Found, 4.63 per cent.

Properties.—The piperonylidene compound forms lustrous brown plates from alcohol, which melt at 178°, and are very slightly soluble in cold, soluble in hot alcohol or tetrachloride of carbon; soluble in amyl alcohol, ethyl acetate, chloroform, or benzene; slightly soluble in gasoline. A solution of ferric chloride, if warmed slightly, turns it dark and splits off piperonal, to judge from the odor.

2-Acetyl-4-cinnamylidenaminonaphthol-1, $C_6H_5CHCHCHNC_{10}H_5(OH)$-$COCH_3$, was prepared by allowing cinnamic aldehyde to stand with the free base in absolute alcohol for thirty minutes. After crystallization from alcohol it melted constantly at 144° The yield was 95 per cent. of the theoretical.

Calculated for $C_{21}H_{17}O_2N$: N, 4.44. Found, 4.51 per cent

Properties.—Brownish yellow needles melting at 144°; slightly soluble in cold, soluble in hot alcohol; soluble in ether, ethyl acetate, tetrachloride of carbon, or benzene. A solution of ferric chloride set free cinnamic aldehyde, to judge by the smell.

Salicylic aldehyde gave a crystallin precipitate with an alcoholic solution of 2-acetyl-4-aminonaphthol-1, similar to those described above.

2-Benzalacetyl-4-nitronaphthol-1, $C_{10}H_5(OH, (COCHCHC_6H_5)NO_2$.—To an alcoholic solution of 10 grams of 2-acetyl-4-nitronaphthol-1 were added the equivalent amount of benzaldehyde and 20 grams of a 30 per cent. solution of sodium hydroxide and the mixture was heated on the steam bath under a return condenser for an hour. The bright red liquid thus obtained, when poured into acidified water, gave an oily precipitate, which soon crystallized. One portion of this red solid was crystallized first from glacial acetic acid and afterward from a mixture of benzene and tetrachloride of carbon; it melted between 203° and 208°. In no case did we succeed in obtaining a sharp melting point with this substance; the temperatures given are those which were not altered by subsequent crystallization. It is possible that this peculiarity of the melting point was in part due to the formation of some azoxy compound by the sodium hydroxide and alcohol, which afterward could not be removed by crystallization, and this would also explain the red color. A specimen of what we think is the same compound made by the nitric acid process (which could contain no azoxy compound) melted at 206–208°, and was orange-yellow; it therefore gives some support to this hypothesis, but it is to be observed that even this is not a sharp melting point. Another portion of the red product was recrystallized from a mixture of benzene and alcohol and melted at 202–206°. It had a reddish orange color.

Calculated for $C_{19}H_{13}O_4N$: N, 4.40. Found, 4.67 per cent.

The azoxy compound, $C_{38}H_{26}N_2O_5$, contains 4.74 per cent. of nitrogen, so that the analysis cannot distinguish between the two formulas.

Properties.—The benzalacetyl compound crystallizes from glacial acetic acid in needles of a bright orange-yellow color; but, if these yellow crystals are allowed to cool in the acid, they turn red. By heating them again with glacial acetic acid their yellow color is restored, the red form reappearing, if they are allowed to cool in the acid, whereas they remain yellow, if filtered and dried before the acid has cooled. We can offer no explanation of this phenomenon. The melting point varied according to the method of purification, 203–208° from benzene and tetrachloride of carbon, 202–206° from benzene and alcohol. Soluble in benzene; slightly soluble in alcohol, even hot, or in tetrachloride of carbon; slightly soluble in cold, much more soluble in hot glacial acetic acid.

What we suppose to be the same compound was prepared from 2-benzalacetylnaphthol-1 as follows: One gram of the ketone dissolved in hot glacial acetic acid was treated with the calculated amount of fuming nitric acid, also dissolved in glacial acetic acid. As the liquid cooled, a heavy, yellow crystallin precipitate was deposited, which, after washing with water and crystallization from a mixture of alcohol and benzene, melted at 206–208°.

Calculated for $C_{19}H_{13}O_4N$: N, 4 40. Found, 4 39 per cent

Properties.—It crystallizes in orange-yellow needles clinging together like fibers of asbestos, which melt at 206–208°, and show the same solubilities as the substance prepared by the other method. An attempt to make a bromine derivative gave a lemon-yellow product, which could not be dried without decomposition. A specimen of the nitro compound was boiled for eight hours with tin, hydrochloric acid and alcohol without reduction, as there was no change in the melting point.

2-Metanitrobenzalacetylnaphthol-1, $C_{10}H_6OHCOCHCHC_6H_4NO_2$.—The condensation of metanitrobenzaldehyde with the ketone was a difficult affair, and we obtained little or no action with aqueous solutions of sodium hydroxide of varying strengths up to 50 per cent. tried under a variety of conditions, and we were no more successful with sodium ethylate, a saturated solution of sodium hydroxide in alcohol, zinc chloride, or barium hydroxide. Sulphuric acid of 66 per cent. gave a product, but it seemed very unmanageable. A small yield of the condensation product was finally obtained by allowing the 2-acetylnaphthol-1 and metanitrobenzalaldehyde to stand for three days at ordinary temperatures with a 20 per cent. solution of potassium hydroxide in alcohol, when a black solid was obtained, which became brownish red on drying. The filtrate from it contained unaltered acetylnaphthol. The solid was treated with water, in which it was slightly soluble, and then acidified with acetic acid, which threw down a dirty orange precipitate. This, after washing, was recrystallized from a mixture of four parts of benzene to one of alcohol, until it showed the constant melting point 210°.

Calculated for $C_{19}H_{13}O_4N$: N, 4.40. Found, 4.59 per cent.

Properties.—The metanitro compound forms red microscopic needles arranged in clusters. Melting point 210°. Soluble in chloroform; slightly soluble in hot glacial acetic acid, or hot alcohol, nearly insoluble in cold alcohol. It absorbs bromine easily, forming a vermilion-colored substance.

2(6-Nitropiperonylalcohol)acetylnaphthol-1, or 1(naphthol-1)-1-keto-3-hydroxy-3(6-nitro-3,4-methylendihydroxyphenyl)-propane, $C_{10}H_6(OH)COCH_2$-$HOCHC_6H_2NO_2(O_2CH_2)$.—This ketol was formed instead of the piperonylidene compound expected, when 5 grams of the 2-acetylnaphthol-1 and 5.3 grams of 6-nitropiperonal were dissolved in hot alcohol, cooled to the temperature of the room, and treated with 25 grams of a 30 per cent. aqueous solution of sodium hydrate. The liquid began to grow dark immediately, and soon became red, depositing a yellow solid The action was promoted by frequent shaking, but heat must be carefully avoided, as it interfered with the success of the process. After four or five hours the dark yellow precipitate was filtered out and acidified with acetic acid. A preliminary washing with water, which was used, is not to be recommended, as the substance is soluble in water to such an extent that it was probably a sodium salt. After the acidification the substance was crystallized from glacial acetic acid till it showed the constant melting point 201–202°.

Calculated for $C_{20}H_{15}O_7N$: C, 62.99, ; H, 3.93, N, 3.67.
Found: C, 62.45, 62.55, H, 2.71, N, 4.03.

An acetate might possibly have been formed by the glacial acetic acid used in purifying the substance, and this would give very nearly the same percentages of carbon, hydrogen and nitrogen as the free ketol; therefore, to prove that our substance was not an acetate, it was boiled for an hour with strong hydrochloric acid and was recovered unaltered at the end of this time. For still greater certainty a sample was purified without the use of glacial acetic acid by crystallizing it from benzene and alcohol, when, with some difficulty, it was obtained with the same melting point and crystallin form.

Properties.—The ketol forms long, lemon-yellow needles which melt at 201–202°. It is moderately soluble in cold acetone, more so in hot; slightly soluble in ether or in cold glacial acetic acid, soluble in hot glacial acetic acid; somewhat soluble in cold, soluble in hot ethyl acetate; very slightly soluble in cold, slightly in hot alcohol; very slightly in cold, moderately in hot benzene; essentially insoluble in tetrachloride of carbon. Strong sulphuric acid dissolves it with a red color, but a yellow precipitate is formed on adding water; strong hydrochloric acid has no effect on it, even when hot; boiling with sodium hydroxide gives the 2-acetylnaphthol-1 to judge from its melting point, 98°.

A saturated alcoholic solution of the ketol turned red, when treated with piperidine, and the color became very dark after boiling for two minutes. This formed with water a red solution with a fine blue fluorescence, from which acidification threw down a yellow precipitate, but this was not studied further. The behavior of the ketol with acetic anhydride and with bromine is described later in the paper.

Monoacetate of the Ketol.—When the 2-(6-nitropiperonylalcohol)-acetylnaphthol-1 was heated in a flask with a return condenser with acetic anhydride for an hour to an hour and a half, and the product, after cooling, poured into water, two products were obtained, an orange one, which proved to be the monoacetate, and a red, which was found to be the flavanone, described later. The orange product was separated from the red by treatment with chloroform, which dissolved it, leaving the red behind. On evaporating the filtered solution the acetate was obtained nearly pure, and was recrystallized from a mixture of alcohol and benzene until it showed the constant melting point 188–190°.

Calculated for $C_{22}H_{17}O_8N$: C, 62.41; H, 4.02.
Found: C, 62.93; H, 5.10.

This analysis is of little value in determining the nature of the substance, as the free ketol contains 62.99 and the diacetate 61.93 per cent. of carbon, but that it was the monoacetate was shown by the analysis of its bromine derivative, described in the next section.

Properties.—The monoacetate crystallizes from glacial acetic acid in cream-colored needles, which melt at 188°–190°. It is soluble in chloroform; moderately soluble in cold, soluble in hot benzene; slightly soluble in cold alcohol, soluble with difficulty when hot; slightly soluble in cold, soluble in hot glacial acetic acid. Boiling with strong hydrochloric acid made it take on a brownish yellow color, but we were unable to raise the melting point of the small amount of product obtained above 188°.

Tribromo Derivative of the Monoacetate of the Ketol.—The monoacetate just described was dissolved in glacial acetic acid, the solution kept hot on the steam bath, and treated with an excess of bromine. When no more hydrobromic acid was given off the product was poured into water and the yellow precipitate thus obtained purified by repeated solution in glacial acetic acid and precipitation with water.

Calculated for $C_{22}H_{14}O_8NBr_3$: Br, 36.36. Found, 36.49 per cent.

The tribromo compound of the free ketol would contain 37.85, of the diacetate 34.98 per cent. of bromine, so there is no doubt that this compound is a monoacetate.

Properties.—The tribromo derivative crystallizes with difficulty from chloroform in small yellow needles. It has no definit melting point, but decomposes between 160 and 170°, although it turns pale green between 110 and 115°. It is moderately soluble in alcohol, or ligroin, when cold, soluble in either solvent if hot; soluble in ether, chloroform, glacial acetic acid, or benzene. After heating with sodium ethylate only a slight test for a bromide—little more than an opalescence was obtained. The bromine is therefore probably not attached to the side chain.

Diacetate of the Ketol.—This substance was obtained when the ketol was boiled with acetic anhydride and sodium acetate instead of with the anhydride alone. After boiling for nearly two hours, water was added which precipitated an oil, soon hardening to a pale greenish yellow solid. This was washed with water and recrystallized from benzene till it showed the constant melting point 197–198°.

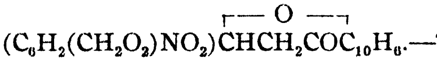
Calculated for $C_{24}H_{19}O_9N$. C, 61 93; H, 4 08.
Found: C, 62 08, H, 5 64.

This analysis shows little, as the ketol and its mono- and diacetate all contain nearly the same percentage of carbon. It has been shown in the introduction to this paper that this substance is either the diacetate or a quinoid form of the monoacetate.

Properties.—The diacetate forms lustrous, golden, rectangular crystals melting at 197–198°. It is somewhat soluble in cold glacial acetic acid, or benzene, tolerably soluble in either of these solvents when hot; essentially insoluble in cold, and only slightly soluble in hot alcohol; slightly soluble in ether.

Action of Bromine on the Ketol.—This work was undertaken so near the end of the term that we have not been able to carry it beyond the preliminary stage. Bromine had no apparent action on the 2-(6-piperonylalcohol)-acetyl-naphthol-1 in the cold in chloroform suspension, but, if the ketole was dissolved in hot glacial acetic acid, and an excess of bromine added, hydrobromic acid was given off, and at the end of two or three minutes' heating on the steam bath an orange precipitate began to form, which soon became so thick that it was necessary to add more acetic acid to the pasty mass. After about three hours' heating on the steam bath, hydrobromic acid ceased to come off and the acetic acid solution was filtered from the orange-red precipitate, which formed the main product of the reaction, while a second yellow substance was obtained by the addition of water to the filtrate. That the two substances are different is shown not only by their melting point (red 252°, yellow 220°), but by their solubilities, the red compound being insoluble or nearly so in all solvents except nitrobenzene; the yellow, soluble in all the solvents tried. Two samples of the red compound gave agreeing amounts of bromine (11.83 and 11.38) on analysis, although one was purified only by washing, the other by precipitation with alcohol from a solution in nitrobenzene, but these numbers stand in no relation we can find to the monobromo ketol, which contains 17.39 per cent. of bromine. The yellow substance could not be purified sufficiently for analysis in the time at our disposal. Neither product gave up any quantity of halogen on treatment with sodium hydroxide.

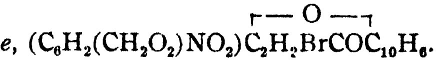
2-(6-Nitro-3,4-methylenedioxyphenyl)-naphthoflavanone,



$(C_6H_2(CH_2O_2)NO_2)\overset{\ulcorner\!-\!-\;O\;-\!-\!\urcorner}{CHCH_2COC_{10}H_6}$.—This substance was made at the same time with the monoacetate by boiling the 2-(6-piperonylalcohol)-acetylnaphthol-1 with acetic anhydride. It was separated from the acetate by dissolving the latter with chloroform, in which the red flavanone was essentially insoluble. It was purified by crystallization from glacial acetic acid, until it showed the constant melting point 226°. As the yield was often very small in this process, a new method for preparing the substance was contrived, which consisted in boiling the ketol with alcohol and zinc chloride for one and a half to two hours, when the red crystals separated in good quantity.

Calculated for $C_{20}H_{13}O_6N$: C, 66.11 H, 3.59.
Found: C, 66.27, 65.95; H, 4.94, 3.39.

Properties.—The flavanone crystallizes in red needles with an orange tinge, which melt at 226°. It is essentially insoluble in ether, chloroform, or ligroin, also in alcohol, benzene, or glacial acetic acid when cold, slightly soluble in hot alcohol, very slightly in hot benzene, and soluble in hot glacial acetic acid. Bromine acts on it with the evolution of hydrobromic acid, as described in the next paragraph.



Bromine Compound of the Flavanone, $(C_6H_2(CH_2O_2)NO_2)\overset{\ulcorner\!-\!-\;O\;-\!-\!\urcorner}{C_2H_2BrCOC_{10}H_6}$. —When the flavanone was suspended in chloroform, or dissolved in glacial acetic acid, and treated with an excess of bromine, hydrobromic acid was given off, and an orange precipitate was thrown down. To purify it for analysis it was washed thoroughly with hot glacial acetic acid, after which it showed a decomposition point between 250° and 255°.

Calculated for $C_{20}H_{12}O_6NBr$: Br, 18.09; found, 17.49, 17.49 per cent.

These analyses are as near, as could be expected, when it is remembered that the substance was purified only by washing.

Properties.—An orange powder decomposing between 250° and 255°. It is essentially insoluble in alcohol, tetrachloride of carbon, or benzene; slightly soluble in hot ethyl acetate or carbon disulphide; very slightly soluble in hot glacial acetic acid, essentially insoluble in all these solvents when cold. A drop of alcoholic potassium hydroxide added to the substance suspended in alcohol turned it red—a very bright red on warming—and gave a good test for potassium bromide. The end of the year prevented us from studying the red products of this reaction.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

1-BENZOYLPHENYL-3-METHYL-5-PYRAZOLONE.[1]

BY HENRY A TORREY AND H. R. RAFSKY.

Received August 27, 1910.

Pyrazolones containing a radical other than phenyl in the 1-position are far from common, and in the present paper we add another member to this small class of compounds. The 1-benzoylphenyl-3-methyl-5-pyrazolone was made (following Michael's general method for making pyrazolones) from the hydrochloride of parahydrazinobenzophenone and acetoacetic ester with a few drops of hydrochloric acid. It melts at 170–171°. Unfortunately, the short time at our disposal prevented us from studying, beside the free base, more than the hydrochloride and the dimethyl compound, of which latter we did not get an analysis. We add an improvement to Döbner's method of making paraminobenzophenone, and several details which we found necessary to insure success in Ruhemann and Blackman's method of making the parahydrazinobenzophenone.

Experimental Part.

The paraminobenzophenone necessary for this work was made according to the method of Döbner[2] by the action of benzoyl chloride on phthalanil in presence of zinc chloride (the purified product being subsequently saponified into the paraminobenzophenone), but we found that the hard, pitch-like substance formed could be worked up with better results by extraction with alcohol, without boneblack, than by the treatment with glacial acetic acid and boneblack recommended by him. For this purpose several hundred grams of the crude substance were boiled with a reflux condenser for some time with 700–800 cc. of alcohol, the solution filtered boiling through a steam funnel, and the filtrate cooled in ice water, when crystals were deposited. By using two portions of alcohol the process could be run continuously, and, although it took more time than that with acetic acid, it gave much less trouble, and the product, while not quite so pure, proved to be sufficiently so for our purpose The paraminobenzophenone prepared from it with potassium hydroxide, after one recrystallization, melted at 124°, as it should; but the principal advantage of this method was that the yield was 170–180 grams as compared with 70–80 grams by the old method.

Parahydrazinobenzophenone was prepared by the method of Ruhemann and Blackmann,[3] consisting in the reduction of the diazo compound with stannous chloride and hydrochloric acid. This process, as was to be expected, gave us much trouble, but we finally succeeded in obtaining the hydrazine by observing the following precautions: The paraminobenzophenone was ground in a mortar with strong hydrochloric acid, so as to obtain a powder fine enough to remain easily in suspension in the hydrochloric acid used for the diazotization. The mixture was cooled carefully with ice and the concentrated solution of sodium nitrite added in five portions at intervals of an hour with frequent shaking. The completion of the reaction was determined by the disappearance of yellow sediment, but a white one always remained.

---

[1] This research was suggested by the late Professor H. A Torrey, and somewhat more than half of the experimental work was done under his direction, but the remainder of the experimental work and the writing of the paper were deprived of the benefit of his supervision by his too early death C. L. JACKSON.

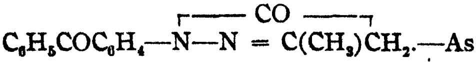
[2] *Ann.*, **210**, 267.

[3] *J. Chem. Soc.*, **55**, 613.

The solution was allowed to stand overnight in ice, filtered, and added slowly, with constant stirring, to the solution of stannous chloride in strong hydrochloric acid (which was also well cooled with ice) at which the yellow precipitate mentioned by Ruhemann and Blackman was formed. This, after standing in the cold solution for half an hour, was filtered and dried on a porous plate. If it was dried on a steam radiator, it turned red, but this red product seemed to give the hydrazine hydrochloride as well as the orange-yellow one which was dried at ordinary temperatures.

The extraction of the hydrochloride from this product gave much trouble. The first extraction with a large amount of warm water could be filtered off without difficulty, but the second converted the residual tin salt into the colloidal state, when it was impossible to remove it by filtering, or decantation. After many experiments this difficulty was overcome as follows: The crude product was warmed with twice its volume of water at 50–60° with shaking for several minutes. As stated by Ruhemann and Blackman, heating to boiling causes some decomposition. It was then filtered rapidly, and by quick work a second similar extraction could be carried through before the precipitate had grown too fine to filter, but, when water was added for the third extraction, a colloidal solution was formed. By the addition of hydrochloric acid to this colloidal solution a precipitate similar to the original was formed which, after being filtered, and pressed on a porous plate, could be extracted three times before it became colloidal, and fortunately this was enough to extract all the hydrochloride of the hydrazine. This was precipitated from the combined water extracts by the addition of hydrochloric acid. The free hydrazine was then obtained by the addition of a concentrated solution of sodium acetate to a warm aqueous solution of the hydrazine hydrochloride. We have given an account of these additional details of the process in the hope of saving others the large expense of time and labor, which we found necessary in order to get a good result.

1-Benzoylphenyl-3-methyl-5-pyrazolone,



$C_6H_5COC_6H_4{-}\overbrace{N{-}N = C(CH_3)CH_2}^{CO}$.—As the method of Knorr[1] for the production of pyrazolones seemed to give a very impure product in this case, we tried to prepare the substance by the general method of Michael,[1] which also had the advantage of using the hydrochloride, and thus avoiding the somewhat wasteful preparation of the free hydrazine. The hydrochloride of the parahydrazinobenzophenone mixed with acetoacetic ester in molecular proportions (a slight excess of the ester does no harm) and a few drops of hydrochloric acid were heated on the steam bath for half an hour. The mixture melted, gave off vapors at first, and was converted into a yellow, pasty mass, which solidified on cooling. It was purified by crystallization from alcohol until it showed the constant melting point 170–171°.

---

[1] *Ber.*, 16, 2597 (1883)

The analyses gave 10.31 and 10.01 per cent. N; calculated for $C_{17}H_{14}O_2N_2$, gives 10.07 per cent. N.

Properties of 1-Benzoylphenyl-3-methyl-5-pyrazolone.—Brownish yellow crystals from alcohol, which melt at 170–171°. Freely soluble in alcohol; rather soluble in benzene; very slightly soluble in ether; almost insoluble in cold, slightly soluble in hot water. Dissolves on warming in strong hydrochloric acid or in an aqueous solution of sodium hydroxide, if not too concentrated. Silver nitrate gives a white flocculent precipitate with an alcoholic solution. The pyrazolone does not reduce Fehling's solution.

Hydrochloride.—The 1-benzoylphenyl-3-methyl-5-pyrazolone was dissolved in benzene and dry hydrochloric acid gas was passed into the solution. The light brown precipitate formed was dried *in vacuo*.

The analysis gave 11.55 per cent. Cl; calculated for $C_{17}H_{14}O_2N_2HCl$, gives 11.27 per cent. Cl

We obtained the salt as a pale brown powder, but the color may have been due to a trace of impurity. At 180° it turns dark, shrivels up at 193°, and melts with decomposition at 196°.

In an attempt to make the 2-3-dimethylpyrazolone corresponding to antipyrine, a method similar to Knorr's[2] was used. Three grams of 1-benzoylphenyl-3-methyl-5-pyrazolone were mixed with 3 grams of methyl iodide and 3 grams of methyl alcohol, and the mixture heated to 100° in a sealed tube for 16 hours. The product, a thick dark brown liquid, was warmed on the steam bath and treated with sulphurous anhydride, which hardened the mass, but produced no perceptible decolorization. After cooling and pulverization it was shaken with a very strong sodium hydroxide solution and then dissolved in benzene; after standing for several days the evaporation of the red-brown solution left an amorphous mass with a few embedded crystals; these were removed and used to inoculate the benzene solution of the amorphous portion, and in this way crystals were obtained which, after a second crystallization (with inoculation), were nearly white. Not enough of this substance could be obtained for analysis, because the end of the year prevented a second preparation, but there seems no question that it is the 1-benzoylphenyl-2,3-dimethyl-5-pyrazolone, from the method of its formation and the fact that ferric chloride gives a dark red color with its aqueous solution. It is very soluble in alcohol, or benzene; somewhat soluble in cold, soluble in hot water; soluble in strong hydrochloric acid. The melting point obtained by us (125°) was probably too low, as the amount at our disposal was too small to make certain of the purity of our specimen.

---

[1] *Am. Chem. J.*, 1892, 517.

[2] *Ber.*, 17, 2032.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

NOTE ON SOME PROPERTIES OF PIPERONYLOIN.

BY HENRY A. TORREY AND J. B. SUMNER.[1]

Received August 27, 1910.

The object of this work was to compare the behavior of piperonyloin and benzoin under similar conditions. The number of results obtained is small, partly because we had but little time at our disposal, but still more because the piperonyloin, $CH_2O_2C_6H_3COCHOHC_6H_3O_2CH_2$, proved to be much less reactive than benzoin; thus no substance corresponding to desoxybenzoin could be obtained under the usual conditions for forming that substance, or a variety of modifications of them. Most of the piperonyloin remained unaltered, the product of the reaction being little more than a trace of what seemed to be a pinacone. No oxime could be made: in fact there was no reaction, as far as we could find, under conditions which give the oxime of benzoin with ease; and no more than a trace of an acetyl compound was formed by long continued and varied action of acetyl chloride on the piperonyloin. These differences between benzoin and piperonyloin form the most important result of this research, but until more observations have been made, it is not worth while to speculate on their cause.

The only substances we have found which react easily with piperonyloin are urea and ammonium thiocyanate. The ureide decomposes at 262°, the thioureide near 260°, but the formula of the latter has not been established by us with certainty.

We also describe a modification of Perkin's method of preparing piperonyloin, which makes it possible to use larger quantities of substance.

Experimental Part.

The piperonyloin used in this work was prepared by the method of Perkin,[2] but we found that we obtained a better result, when instead of heating the mixture of 5 grams piperonal, 20 grams of 50 per cent. alcohol, and 2 grams of potassium cyanide for 6–8 hours, as recommended by him, the heating was carried on for only 3 hours, or the materials were allowed to stand at ordinary temperatures a few days. Under these latter conditions a yield of 80 per cent. of crude piperonyloin was obtained from 100 grams of piperonal, whereas Perkin states that the amount of piperonal used must be restricted to 5 grams in order to get a good result.

---

[1] This research was suggested by the late Professor H. A. Torrey, and somewhat more than half of the experimental work was done under his direction, but the remainder of the experimental work and the writing of the paper were deprived of the benefit of his supervision by his too early death. C. L. JACKSON.

[2] *J. Chem. Soc.*, 59, 164.

Treatment of piperonyloin with zinc and 80 per cent. alcohol, saturated with hydrochloric acid, under the same conditions, which give desoxybenzoin, gave on dilution a black tar, which could not be purified by distillation. Treatment with ether dissolved the tarry impurities, leaving a mass of yellow crystals, which proved to be unaltered piperonyloin, and made up the greater part of the product. It follows, therefore, that piperonyloin is much less affected by this reducing agent than benzoin. On trying to distil under a pressure of 1.5 cm. the tar obtained from the ether, a drop of distillate came over at 110°, and after this nothing till 246°, when about two-thirds of the substance passed over, leaving a black viscid mass. By crystallization of this distillate a body melting at 170° was obtained, probably a pinacone, but we did not obtain it in sufficient quantity for investigation. Many of the reducing processes were tried, but with no success.

According to Goldschmidt and Polonowska,[1] the oxime of benzoin is obtained with no difficulty; but with the piperonyloin we could obtain no reaction, although the conditions were varied in a number of different ways. In every case the piperonyloin was recovered unaltered.

Zinin[2] made the acetate of benzoin by heating it with acetyl chloride at 40-50° and finally at 100°, until there was no more action. Piperonyloin gave no perceptible action with acetyl chloride under these conditions, or any others we could find. By extracting the product with ether, in which piperonyloin is nearly insoluble, a trace of a yellow substance melting near 135° was obtained, but the quantity was so small that it was useless to think of obtaining enough for study.

Piperonyloinureide, $C_{17}H_{12}O_5N_2$.—This substance was made by heating 5 grams of piperonyloin with an excess of urea and amyl alcohol in a sealed tube at about 190° for three hours. The tube contained some large crystals and a black liquid. The crystals were washed with cold water and recrystallized four times from glacial acetic acid, after which the acid was washed off with alcohol and the substance dried at 110° for analysis.

The analyses gave 7.78 and 8.90 per cent. N; calculated, 8.64 per cent.

Properties.—The ureide forms pale pinkish crystals, as obtained by us, which decompose at about 265°. The substance is slightly soluble in hot alcohol, moderately soluble in hot amyl alcohol; slightly soluble in cold, very soluble in hot glacial acetic acid; essentially insoluble in water, or benzene, even if hot.

---

[1] *Ber.*, **20**, 492.

[2] *Ann.*, 104, 120.

The *thioureide* was prepared by heating piperonyloin with an excess of ammonium thiocyanate in a sealed tube to 170°. The crystals obtained in this way were washed with cold water and purified by crystallization from hot methyl alcohol.

The analyses gave 8.61 and 8.50 per cent. S; calculated for $C_{17}H_{12}O_4N_2S$, 9.41; for $C_{17}H_{14}O_5N_2S$, 8.99.

The analyses cannot distinguish between the two formulas, and we are inclined to adopt the first in spite of the fact that it agrees less well with the percentages found than the second, since this formula is analogous to that of the ureide, and the difference in results might be caused by a little of some impurity, which could not be removed from the small amount of substance at our disposal.

Properties.—The thioureide crystallizes in long, felted, nearly white needles, which decompose near 260°; slightly soluble in ethyl alcohol, methyl alcohol, acetone, or glacial acetic acid, when cold; moderately soluble in hot methyl alcohol, or carbon disulphide; very soluble in pyridine; insoluble in water.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 182.]

SOME DERIVATIVES OF *p*-AMINOBENZONITRILE.

BY MARSTON TAYLOR BOGERT AND LOUIS ELSBERG WISE.

Received September 11, 1910.

In 1903, Bogert and Kohnstamm[1] published a brief article on *p*-aminobenzonitrile, giving its method of preparation and properties, and describing also its acetyl and propionyl derivatives.

The present paper is a continuation of this work. In it are described improved methods for the production of the *p*-nitro- and *p*-aminobenzonitriles and of the acetyl derivative of the latter, as well as certain new substances.

By the action of glacial formic acid, of benzoyl chloride, and of benzenesulphonyl chloride, upon the aminonitrile, the corresponding acyl derivatives were obtained, while with oxalic esters, cyano-oxanilic esters and cyano-oxanilide were secured. The acetaminonitrile yielded the acetaminobenzamide with alkaline hydrogen dioxide, and the *m*-nitro-*p*-acetaminobenzonitrile on direct nitration. By reduction of the latter, the 3,4-diaminobenzonitrile was prepared, a most interesting orthodiamine.

The work is being continued and another paper will appear shortly. The fact that other chemists are working in closely related fields, or are approaching this field from other directions, has made it seem to us advisable to publish this preliminary paper.

---

[1] THIS JOURNAL, 25, 478 (1903)

Experimental.

p-Nitrobenzonitrile, $(4)O_2N.C_6H_4.CN(1)$, is best prepared by the well-known Sandmeyer method[1] from pure *p*-nitroaniline. It may be prepared also from the commercial "Nitrosamine" paste.

The latter, placed at our disposal through the courtesy of the Badische Company, contains about 25 per cent. of the sodium salt of *p*-nitrophenylnitrosamine mixed with the necessary amount of nitrite[2] and was converted into the diazo compound by mixing 60 parts of the paste with 200 parts cold (not over 18°) water, then adding 21 parts dilute hydrochloric acid (about 30 per cent. HCl) in a fine stream, stirring gently. This diazo solution was allowed to stand for about a half hour, with occasional gentle stirring, was filtered (from diazoamino compounds and other contaminants), and the filtrate added to the copper cyanide solution in the usual way. The temperature of the diazo solution must at no time rise above 18°. The crude nitronitrile was separated from mineral salts by extraction with boiling carbon tetrachloride. Orange crystals were thus obtained, which were still impure. The yield of these orange crystals varied from about 31 to 43 per cent. of the theory. Further purification was effected by recrystallization from water, distillation with steam, or sublimation.

A much more satisfactory method is to distil the original crude nitrile direct with steam. The product thus obtained is practically pure (m. p. about 148°, cor.), and the yield about 50 per cent. of the theory if pure *p*-nitroaniline was used as the initial material.

The pure nitronitrile forms nearly colorless, fluffy crystals, melting at 147.5-8.5° (cor.). It is soluble in water, acetic acid, chloroform, and carbon tetrachloride, at their boiling points, volatil with steam, and can be sublimed. It has an odor recalling that of a mixture of nitrobenzene and benzonitrile.

p-Aminobenzonitrile, $(4)H_2N.C_6H_4.CN(1)$.—The nitronitrile was reduced with stannous chloride and hydrochloric acid.[3] It is important that a pure nitronitrile be used in this reduction, as it is not so easy to separate the aminonitrile from impurities, and the yield is thus considerably decreased. After reduction, no excess of concentrated hydrochloric acid was added, but the mixture was left in the refrigerator overnight, the separated tin double salt of the aminonitrile then filtered out, dissolved in cold water in a separatory funnel, ice and ether added, the solution carefully made alkaline with dilute ice-cold sodium hydroxide solution, and the mixture well shaken. The ethereal layer was separated, and the extraction with ether repeated several times. The ethereal extracts were united and the ether driven off, leaving the aminonitrile in deeply colored crystals. Purified by recrystallization from water, it was obtained in colorless needles or long prisms. The best yield of aminonitrile was about 75–6 per cent. of the theory.

---

[1] Bogert and Kohnstamm, THIS JOURNAL, **25**, 479 (1903).

[2] *Ber.*, **27**, 514 (1894); U. S. Patents 531973, 531974, 531975, 531976 and 531977.

[3] Bogert and Kohnstamm, *Loc cit.*; Bogert and Hand, THIS JOURNAL, **24**, 1033 (1902); Bogert and Beans, *Ibid.*, **26**, 469 (1904).

An attempt to prepare the aminonitrile by distilling a dry and intimate mixture of potassium cyanide and potassium sulphanilate proved unsatisfactory.

The pure aminonitrile forms colorless crystals, melting at 85.5–86° (cor.), as reported by Bogert and Kohnstamm.[1]

p-Formaminobenzonitrile, $(4)HCONH.C_6H_4.CN(1)$, from the nitrile and glacial formic acid, was purified by repeated crystallization from water and decolorization with boneblack. It forms small colorless crystals, melting at 188–9° (cor.) in a sealed tube.

Found: N, 19.31. Calculated for $C_8H_8ON_2$: N, 19.18.

p-Acetaminobenzonitrile, as stated, was described in the paper of Bogert and Kohnstamm.[1] The following is a somewhat better method of preparation:

The aminonitrile is added gradually to an excess of hot acetic anhydride and the mixture heated for ten or twenty minutes. The excess of anhydride is then destroyed by the addition of water to the hot solution and, on cooling, the acetyl derivative crystallizes out practically pure. A small additional amount, less pure, may be recovered from the mother liquor. Yield, 77–85 per cent. of the theory. Crystallized from water until the melting point remained constant, colorless needles were obtained, melting at 205.5° (cor.). Bogert and Kohnstamm[1] found an uncorrected melting point of 200°.

p-Acetaminobenzamide, $CH_3CONH.C_6H_4.CONH_2$.—*p*-Acetaminobenzonitrile was added to a solution of hydrogen dioxide made slightly alkaline with potassium hydroxide, and the mixture heated for half an hour or an hour at 100°. A clear yellow solution resulted. This was filtered hot and the filtrate allowed to cool. The amide which separated was recrystallized first from water and then twice from dilute alcohol. It forms colorless prisms, melting at about 274.5°, with preliminary softening and sublimation. Further crystallization did not alter this melting point or diminish sensibly the tendency to a preliminary drag and sublimation.

Found: N, 15.95. Calculated for $C_9H_{10}O_2N_2$: N, 15.73.

Heated with potassium hydroxide solution, it is saponified with evolution of ammonia.

---

[1] *Loc. cit.*

3-Nitro-4-acetaminobenzonitrile, $(4)CH_3CONH.C_6H_3(NO_2)(3)CN(1)$.—Five grams *p*-acetaminobenzonitrile were gradually stirred into a paste prepared by adding 6.7 g. finely pulverized potassium nitrate to 30 cc. concentrated sulphuric acid, and the whole kept at a temperature of —10° to 0° by a freezing mixture. After all the nitrile had been added, the mixture was held at about 0° for an hour or two longer, and the sirupy mass then poured slowly upon cracked ice. After standing for a short time, the yellow precipitate was washed with water, a little very dilute ammonium hydroxide solution, and again with water. Without previous drying, it was added to warm acetic anhydride, the solution boiled for a few minutes, water added to destroy the excess of anhydride, and on cooling the nitrile separated in beautiful yellow prisms. Recrystallized from 95 per cent. alcohol, long, lustrous, pale-yellow needles were obtained, melting at 131.5° (cor.), softening somewhat at 130°. Yield, about 64 per cent. of theory. The crystals are soluble in water or alcohol, less readily in benzene, and practically insoluble in carbon tetrachloride.

Found: N, 20.74. Calculated for $C_9H_7O_3N_3$: N, 20.49.

The process just described must be followed closely to get a good yield of pure substance. We have tried various other methods of nitration, but none proved as satisfactory as the above.

To locate the nitro group, the nitroacetaminobenzonitrile was saponified by boiling it with alcoholic potassium hydroxide solution. During the boiling, ammonia was evolved and the solution turned purple. On cooling, orange needles separated, corresponding in properties to the description in the literature of potassium 3-nitro-4-aminobenzoate. The free acid liberated from this salt by the action of hydrochloric or sulphuric acid crystallized from dilute alcohol in orange-yellow needles which, carefully dried in vacuum and heated in a sealed tube, began to sublime at about 190–200°, forming a yellow coating on the sides of the tube. At 277–8° (cor.), the sides of the tube began to clear, and at 290–1° (cor.) the substance decomposed. Salkowski[1] and Ritsert[2] give the melting point of 3-nitro-4-aminobenzoic acid as 284°.

Found: N, 15.05 and 15.27 Calculated for $C_7H_6O_4N_2$, 15.39.

As a further check on the correctness of the work, some 3-nitro-4-aminobenzoic acid was prepared according to the method of Ritsert[3] by nitrating pure *p*-acetaminobenzoic acid, and the product was found to be identical with that obtained by the saponification of the above nitroacetaminobenzonitrile.

p-Benzoylaminobenzonitrile, $C_6H_5CONH.C_6H_4.CN$, from *p*-aminobenzonitrile and benzoyl chloride, in presence of sodium carbonate, was purified by crystallization from dilute alcohol, after treating with boneblack. The pure substance melts at 170°–170.5° (cor.), with very slight previous softening.

---

[1] *Ann.*, 173, 54.

[2] D. R. P., 151725.

[3] *Loc. cit.*

Found: N, 12.94 and 12.78. Calculated for $C_{14}H_{10}ON_2$: N, 12.62.

p-Benzenesulphoneaminobenzonitrile, $C_6H_5SO_2NH.C_6H_4CN$.—*p*-Aminobenzonitrile was heated for a few minutes with excess of benzenesulphone chloride. The crude product was washed with ether and crystallized from alcohol to constant melting point. Colorless arborescent crystals, melting at 175–6° (cor.), with very slight preliminary softening.

Found: N, 10.90; S, 12.74. Calculated for $C_{13}H_{10}O_2N_2S$: N, 10.85; S, 12.42.

Methyl p-Cyano-oxanilate, $CH_3OCOCONH.C_6H_4.CN$.—A mixture of 4 g. methyl oxalate and 1.5 g. *p*-aminobenzonitrile was heated for three and a half hours at 110°. The crude product crystallized from methyl alcohol in nacreous leaflets, melting at 208.5–9.5° (cor.).

Found: N, 14.0. Calculated for $C_{10}H_8O_3N_2$: N, 13.73.

Ethyl p-Cyano-oxanilate, prepared similarly to the methyl ester, crystallizes from alcohol in small, nearly colorless, flat prisms, softening somewhat at 187° (cor.), and melting at 188.5–9° (cor.).

Found: N, 13.13. Calculated for $C_{11}H_{10}O_3N_2$: N, 12.85.

Di-p-cyano-oxanilide, (*p*)$NC.C_6H_4.NHCOCONH.C_6H_4.CN$(*p*).—A mixture of equal parts by weight of *p*-aminobenzonitrile and ethyl oxalate was heated five and a half hours at 160–210°. Ethyl *p*-cyano-oxanilate was extracted from the crude product with alcohol, and the residual insoluble product dried and analyzed:

Found: N, 19.33. Calculated for $C_{16}H_{10}O_2N_4$: N, 19.32.

The compound melts above 288°, and is insoluble or very difficultly soluble in water, alcohol, glacial acetic acid, ether, benzene, nitrobenzene, aniline, amyl alcohol or phenol.

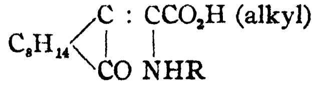
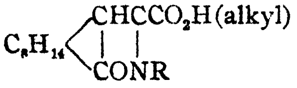
3,4-Diaminobenzonitrile, $(3,4)(NH_2)_2C_6H_3.CN$.—Five grams 3-nitro-4-acetaminobenzonitrile were added gradually to a solution of 35 g. stannous chloride in 75 cc. concentrated hydrochloric acid at a temperature of 30–40°. Complete solution resulted, the deep yellow color gradually growing paler. Nothing separated from this solution even after standing in the refrigerator for several days. It was, therefore, poured into a separatory funnel, covered with a layer of ether, and carefully made alkaline by adding cold dilute sodium hydroxide solution. A voluminous precipitate appeared, not easily soluble in the ether. The mixture was repeatedly extracted with ether, the extracts combined, dried with calcium chloride, and the ether driven off. The colorless residue, dried in vacuum, rapidly turns pink in the air. Crystallized from water, it forms colorless needles, softening at 146° and melting at 147.5° (cor.). This melting point could not be changed by further recrystallization. The compound is soluble in boiling water, hot alcohol or boiling chloroform, but dissolves in ether with difficulty.

Found: N, 31.64. Calculated for $C_7H_7N_3$: N, 31.58.

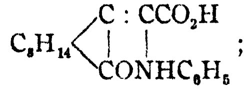
DERIVATIVES OF CAMPHOROXALIC ACID. XIII.[1]

By J. Bishop Tingle and S. J. Bates.

Received September 10, 1910.

In some of the earlier papers on this subject it has been pointed out that the condensation compounds of camphoroxalic acid and of its esters with amines may be formulated either as  $C_8H_{14}\left\langle\begin{array}{l}C : CCO_2H\ (alkyl)\\ |\quad\ \ |\\ CO\ NHR\end{array}\right.$ I., or  $C_8H_{14}\left\langle\begin{array}{l}CHCCO_2H(alkyl)\\ |\quad\ \ |\\ CONR\end{array}\right.$ II. The balance of evidence being in favor of the first of these formulas, it has been employed by the senior author and his colleagues in their publications.

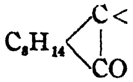
The work described in the present communication had, for one of its objects, the accumulation of more direct positive proof of the constitution of the amino condensation compounds in question; we therefore directed our attention to the investigation of reactions which should show the presence of an imino —NHR, or hydroxyl $>C(OH)—$ group in the condensation compounds.

Our first experiments were carried out with phenylcamphoformeneaminecarboxylic acid,  $C_8H_{14}\left\langle\begin{array}{l}C : CCO_2H\\ |\quad\ \ |\\ CONHC_6H_5\end{array}\right.$; it is prepared very readily from camphoroxalic acid and aniline, is easy to purify and is relatively stable. We obtained it by a slight modification of the method described by the senior author and A. Tingle.[2] The acid is attacked immediately by bromine, in chloroform solution; hydrobromic acid is evolved in quantity, 3,4-dibromoaniline hydrobromide is deposited in crystals and the solution contains camphoroxalic acid. The probable mechanism of this reaction appears to be the more simple on the assumption of the first of the above formulas for phenylcamphoformeneaminecarboxylic acid, although it is by no means conclusive. The readiness with which the hydrogen atoms of the benzene nucleus undergo substitution is noteworthy.

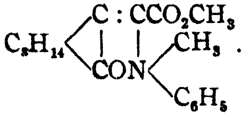
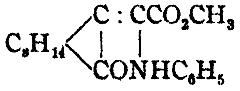
---

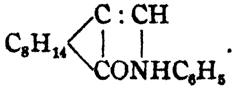
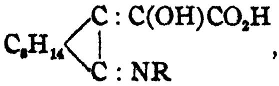
[1] The previous communications of this series have appeared as follows: Bishop Tingle, *Inaug. Dissn.*, Munich, 1889, p. 34; *J. Chem. Soc.*, **57**, 652 (1890); *Am. Chem. J.*, **19**, 393 (1897); **20**, 318 (1898). Bishop Tingle and A. Tingle, *Ibid.*, **21**, 238 (1899); **23**, 214 (1900). Bishop Tingle, This Journal, **23**, 363 (1901). Bishop Tingle and W. E. Hoffmann, *Amer. Chem. J.*, **34**, 217 (1905) Bishop Tingle and C. J. Robinson, *Ibid.*, **36**, 223 (1906). Bishop Tingle, This Journal, **29**, 1242 (1907). Bishop Tingle and L. F. Williams, *Amer. Chem. J.*, **39**, 105, 277 (1908).

[2] *Loc. cit.*

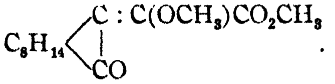
Chromic anhydride, in acetone or in acetic anhydride solution, at the ordinary temperature, is without appreciable effect on phenylcamphoformeneaminecarboxylic acid, but potassium permanganate, dissolved in moist acetone, oxidizes it to camphorquinone. As camphoroxalic acid itself has been shown to suffer attack at the position of the double linkage, it is probable that this reaction follows a similar course, the molecule of the carboxylic acid suffering dissolution into the complexes  $C_8H_{14}\left\langle\begin{array}{l}C<\\ |\\ CO\end{array}\right.$ and $>C(NHC_6H_5)CO_2H$, the former of which then yields the quinine.

The only product which could be obtained by the action of phosphorus trichloride on phenylcamphoformeneaminecarboxylic acid was camphoroxalic acid. Phosphorus pentachloride reacts like the trichloride, ultimately, therefore, the reaction may be expressed as one of simple hydrolysis of the CN linkage

A considerable number of experiments were made, under varying conditions, on the interaction of methyl sulphate and phenylcamphoformeneaminecarboxylic acid. It was, of course, to be expected that a methyl group would replace the hydrogen of the carboxyl, so giving the methyl ester, but we hoped that, in addition, the hydrogen of the $—NHC_6H_5$ (formula I) might be substituted, thus giving the compound  $C_8H_{14}\left\langle\begin{array}{l}C:CCO_2CH_3\\ |\quad\ |\\ CON\left\langle\begin{array}{l}CH_3\\ C_6H_5\end{array}\right.\end{array}\right.$. This would afford direct evidence in favor of the formula in question. Unfortunately, this double substitution could not be realized, the only product which we could obtain was *methyl phenylcamphoformeneaminecarboxylate*,  $C_8H_{14}\left\langle\begin{array}{l}C:CCO_2CH_3\\ |\quad\ |\\ CONHC_6H_5\end{array}\right.$ It is deposited in yellow crystals, melting at 127°. Under the varied conditions of our experiments it does not react with methyl sulphate.

We failed to obtain any reaction between methyl sulphate and phenyl camphoformeneamine,  $C_8H_{14}\left\langle\begin{array}{l}C:CH\\ |\quad\ |\\ CONHC_6H_5\end{array}\right.$. These results, apart from other evidence, appear, therefore, to decide effectively against any formula such as  $C_8H_{14}\left\langle\begin{array}{l}C:C(OH)CO_2H\\ |\\ C:NR\end{array}\right.$, for the condensation products of camphoroxalic acid and amines.

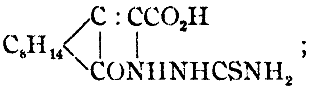
Methyl sulphate and camphoroxalic acid give the methyl ester. On one occasion, by the further action of the sulphate, this ester yielded a small quantity of what appears to be methyl methoxycamphoroxalate,



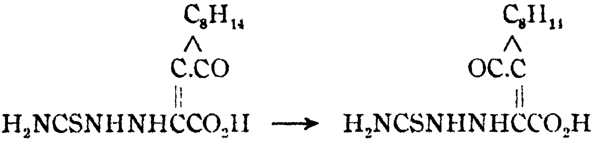
. Hitherto we have not succeeded in obtaining this substance in quantity sufficient for adequate study.

Attempts to obtain compounds from nitrous acid and phenyl camphoformeneaminecarboxylic acid, camphoroxalic acid, or its ethyl ester were unsuccessful. We employed sodium nitrite and also amyl nitrite, under varied conditions.

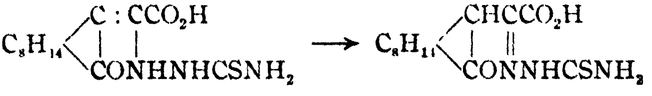
Camphoroxalic and thiosemicarbazine react readily in hot alcohol, more slowly at the ordinary temperature, to form *thiosemicarbazylcamphoformeneaminecarboxylic acid*,



; in benzene, the combination occurs much more slowly at the boiling point of the solution and is inappreciable at the ordinary temperature. The acid exists in two modifications which melt at 120–5° and 148–9°, respectively. The lower melting form (A) is the more readily soluble in benzene, it is somewhat viscid and is produced by adding hydrochloric acid to an aqueous solution of the sodium salt of the carboxylic acid. It is also formed by recrystallizing the higher melting modification (B) from water. It changes slowly at the ordinary temperature, more rapidly when heated alone or with benzene, to the (B) form. A mixture of (A) and (B) melts at 140–5°. The modes of formation of (A) and (B) suggest that the former is an unstable hydrate of the latter. From the nature of the case it is impossible to determine this fact with certainty. There are also the possibilities of *cis-* and *trans-*isomerism,



and of tautomerism,

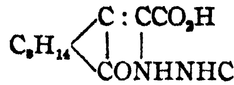
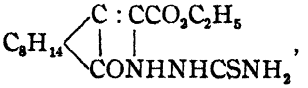


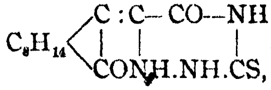
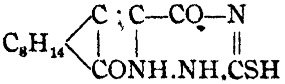
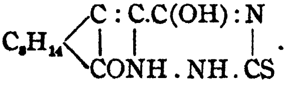
to be considered.

Our chief object in preparing thiosemicarbazylcamphoformeneaminecarboxylic acid was to compare its behavior with the similar derivative of semicarbazine,[1] *i. e.*, to determine the effect of exchanging an oxygen for a sulphur atom. The contrast between the two compounds is most marked in the relative readiness with which they form closed chain derivatives. Whereas semicarbazylcamphoformeneaminecarboxylic acid,

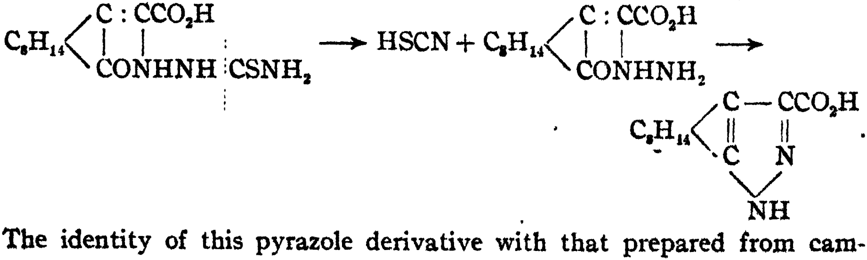
---

[1] Bishop Tingle and Robinson, *Loc. cit.*


$C_8H_{14}<\begin{matrix}C:CCO_2H\\ CONHNHCONH_2\end{matrix}$, undergoes further condensation without difficulty, the thio derivative exhibits comparatively little tendency to change in this direction. When fused, a portion of the acid is recovered and the remainder is converted into resinous products. Absolute alcohol and dry hydrogen chloride give only *ethyl thiosemicarbazylcamphoformeneamine-carboxylate*, 
$C_8H_{14}<\begin{matrix}C:CCO_2C_2H_5\\ CONHNHCSNH_2\end{matrix}$, which is deposited from benzene in white crystals, melting at 150–1°.

Thiosemicarbazylcamphoformeneaminecarboxylic acid is dehydrated by the action of acetic anhydride, quickly at about 100°, more slowly at the ordinary temperature. The yield is almost quantitative and the compound is deposited in bright red crystals, melting at 181–2°. When treated with a warm aqueous solution of potassium hydroxide or a boiling aqueous solution of sodium carbonate the parent acid is regenerated. These reactions make us inclined to regard the compound as being *thiosemicarbazylcamphoformeneaminecarboxylactimide*, 
$C_8H_{14}<\begin{matrix}C:C-CO-NH\\ CONH.NH.CS\end{matrix}$, its deep color, which appears to be characteristic of the compound itself and not due to traces of ferric thiocyanate, suggests that it probably exists in a tautomeric form, such as 
$C_8H_{14}<\begin{matrix}C:C-CO-N\\ CONH.NH.CSH\end{matrix}$ or 
$C_8H_{14}<\begin{matrix}C:C.C(OH):N\\ CONH.NH.CS\end{matrix}$.

Acetic anhydride, to which a few drops of conc. sulphuric acid have been added, hydrolyzes thiosemicarbazylcamphoformeneaminecarboxylic acid to thiocyanic acid, the presence of which was shown by means of a ferric salt, and aminocamphoformeneaminecarboxylic acid, which latter then condenses to camphylpyrazolecarboxylic acid (m. p. 261–2°),


$$C_8H_{14}<\begin{matrix}C:CCO_2H\\ CONHNH\vdots CSNH_2\end{matrix} \longrightarrow HSCN + C_8H_{14}<\begin{matrix}C:CCO_2H\\ CONHNH_2\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C-CCO_2H\\ C\quad N\\ NH\end{matrix}.$$

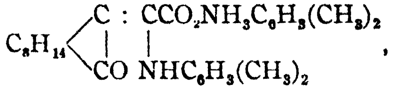
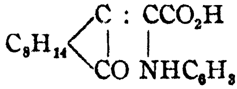
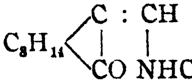
The identity of this pyrazole derivative with that prepared from camphoroxalic acid and hydrazine, or semicarbazine by Bishop Tingle and Robinson,[1] was shown by direct comparison. Our acid melted at 261–2°, whereas the melting point observed previously was 255–8°. The difference is undoubtedly due to variation in the rapidity of heating, because the carboxylic acid evolved carbon dioxide at a temperature below its melting point.[1]

---

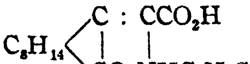
[1] *Am. Chem. J.*, 36, 259.

A slight modification of Bishop Tingle and Robinson's process for the preparation of camphylpyrazolecarboxylic acid is described in the experimental portion of this paper (vide p. 1511).

Only resinous products could be obtained by the action of concentrated sulphuric acid alone, at the ordinary temperature, on thiosemicarbazylcamphoformeneaminecarboxylic acid. We propose to make a further examination, under other experimental conditions, of the ability of this carboxylic acid to form cycloids containing sulphur.

In the hope of obtaining material suited for further investigation, we have examined the interaction of camphoroxalic acid with a number of amines. With 1,3,4-xylidine it gives *1,3,4-xylidine 1,3,4-xylidylcamphoformeneaminecarboxylate*,  $C_8H_{14}\left<\begin{array}{l}C : CCO_2NH_3C_6H_3(CH_3)_2\\ | \qquad |\\ CO\ NHC_6H_3(CH_3)_2\end{array}\right.$, which is deposited in brown crystals, melting at 93–4°. By the action of sodium carbonate, followed by hydrochloric acid, on this salt, *1,3,4-xylidylcamphoformeneaminecarboxylic acid*,  $C_8H_{14}\left<\begin{array}{l}C : CCO_2H\\ | \qquad |\\ CO\ NHC_6H_3(CH_3)_2\end{array}\right.$, is produced. The acid is deposited in yellow crystals, melting at 117–8°. The third member of the series, the amine,  $C_8H_{14}\left<\begin{array}{l}C : CH\\ | \qquad |\\ CO\ NHC_6H_3(CH_3)_2\end{array}\right.$, is probably formed at a temperature above the melting point of the acid, but it could not be isolated in a crystalline condition.

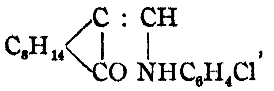
Comparing these compounds with the corresponding derivatives of aniline, it is evident that they crystallize with greater difficulty and are, therefore, less suited for our projected investigations.

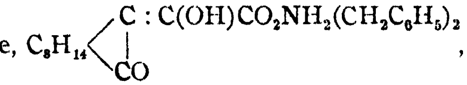
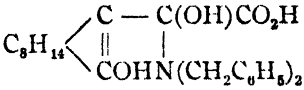
p-Chloroaniline and camphoroxalic acid combine readily to form *p-chlorophenylcamphoformeneaminecarboxylic acid*,  $C_8H_{14}\left<\begin{array}{l}C : CCO_2H\\ | \qquad |\\ CO\ NHC_6H_4Cl\end{array}\right.$, which was obtained in yellow needles, melting at 182–3°. Its crystallizing power is considerable. With a larger proportion of *p*-chloroaniline it failed to form a *p*-chloroaniline salt, although possibly one could be obtained at a low temperature.

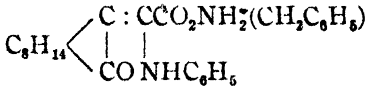
When camphoroxalic acid and *p*-chloroaniline are heated gradually up to 155–60°, without a solvent, carbon dioxide is evolved and *p-chloro-*

---

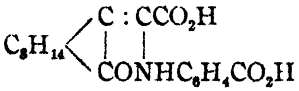
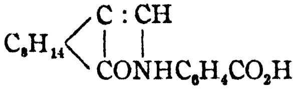
[1] *Loc cit.*

phenylcamphoformeneamine,  $C_8H_{14}\left\langle\begin{array}{l}C : CH\\ |\quad\ \ |\\ CO\ NHC_6H_4Cl\end{array}\right.$, is produced. It is also formed by heating *p*-chlorophenylcamphoformeneaminecarboxylic acid above its melting point. The amine is deposited in white crystals, melting at 194–5°.

Dibenzylamine and camphoroxalic acid react quickly, in equimolecular proportion, to form an additive compound. It gives an intense reddish purple color with an alcoholic solution of ferric chloride and is resolved somewhat slowly into its constituents by the action of an aqueous solution of sodium carbonate, or by hydrochloric acid. In spite of the slowness of this decomposition, we regard the substance as being dibenzylamine camphoroxalate,  $C_8H_{14}\left\langle\begin{array}{l}C : C(OH)CO_2NH_2(CH_2C_6H_5)_2\\ |\\ CO\end{array}\right.$, rather than an acid condensation product such as  $C_8H_{14}\left\langle\begin{array}{l}C - C(OH)CO_2H\\ \|\quad\ \ |\\ COHN(CH_2C_6H_5)_2\end{array}\right.$. See Bishop Tingle and Williams.[1] The compound is deposited in white crystals, melting at 135–6°. It is also formed by the action of 2 molecular proportions of dibenzylamine on camphoroxalic acid.

When dibenzylamine camphoroxalate is heated with aniline (2 mols.) and benzene, under pressure, at 100°, it is converted into *dibenzylamine phenylcamphoformeneaminecarboxylate*,  $C_8H_{14}\left\langle\begin{array}{l}C : CCO_2NH_2(CH_2C_6H_5)_2\\ |\quad\ |\\ CO\ NHC_6H_5\end{array}\right.$, which was obtained in white crystals, melting at 185°. Its composition and nature is established both by its mode of formation and by the fact that it is decomposed into dibenzylamine and phenylcamphoformeneaminecarboxylic acid, when treated with dilute hydrochloric acid.

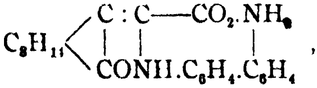
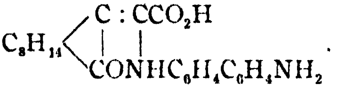
The dibenzylamine camphoroxalate described above, when fused for some time, gives the dibenzylcamphoformeneamine described by Bishop Tingle and Williams.[2] It is also produced when a mixture of camphoroxalic acid and dibenzylamine is heated at 135–40°. The use of 2 molecular proportions of dibenzylamine is without effect on the nature of the product.

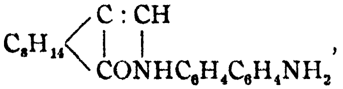
m-Aminobenzoic acid and camphoroxalic acid form *m-carboxyphenylcamphoformeneaminecarboxylic acid*,  $C_8H_{14}\left\langle\begin{array}{l}C : CCO_2H\\ |\quad\ |\\ CONHC_6H_4CO_2H\end{array}\right.$; it is deposited in white crystals, melting at 136–7°. This acid is hydrolyzed rather easily to its constituents; when heated at its melting point carbon dioxide is evolved; the other product of the reaction consists of *m-carboxyphenylcamphoformeneamine*,  $C_8H_{14}<\begin{matrix}C:CH\\ |\quad|\\ CONHC_6H_4CO_2H\end{matrix}$. It is deposited in long yellow needles, melts at 116–7° and dissolves completely in a cold aqueous solution of sodium carbonate.

---

[1] *Am. Chem. J.*, 39, 113.

[2] *Ibid.*, 39, 117.

Bishop Tingle and Hoffman[1] described a condensation compound of benzidine and camphoroxalic acid which they found to melt at 190°. We have repeated this work, but have observed that better results are obtained, as regards the purity of the product, by the use of benzene as the solvent. Our condensation compound was obtained in yellow crystals, which melted at 208°. The melting point of the substance varies considerably with the rate of heating, but the identity of the two specimens was shown by their melting point when mixed. The compound is only slowly dissolved by boiling with aqueous solutions of potassium hydroxide, or of sodium carbonate and it is reprecipitated on acidifying the solutions. This behavior suggests that it is an *inner salt*,  $C_8H_{14}<\begin{matrix}C:C\text{—}CO_2.NH_3\\ |\quad|\qquad\quad|\\ CONH.C_6H_4.C_6H_4\end{matrix}$, rather than *benzidylcamphoformeneaminecarboxylic acid*,  $C_8H_{14}<\begin{matrix}C:CCO_2H\\ |\quad|\\ CONHC_6H_4C_6H_4NH_2\end{matrix}$.

When this salt (or acid) is heated at its melting point, water and carbon dioxide are evolved and *benzidylcamphoformeneamine*,  $C_8H_{14}<\begin{matrix}C:CH\\ |\quad|\\ CONHC_6H_4C_6H_4NH_2\end{matrix}$, is obtained, but it is prepared more conveniently by mixing the salt (or acid) with nitrobenzene and heating at 150–5°. The amine is deposited in crystals, melting at 317–8°.

Camphylamine and camphoroxalic acid react readily, but the product is mostly resinous under the conditions which we employed. We succeeded, however, in isolating a white crystalline *compound*, which melted at 105°. It appears to be formed by the condensation of the constituents, because it dissolves readily in an aqueous solution of sodium carbonate, at the ordinary temperature, and gives no coloration with an alcoholic solution of ferric chloride. Its quantity was too small for further investigation.

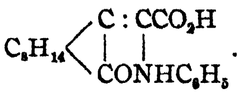
Only resinous substances could be obtained from *p*-aminobenzaldehyde and camphoroxalic acid.

Experimental.

Preparation and Reactions of Phenylcamphoformeneaminecarboxylic

---

[1] *Am. Chem. J.*, 34, 231–50.

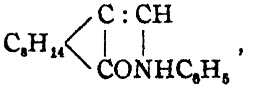
Acid,  $C_8H_{14}\!<\!\begin{matrix}C:CCO_2H\\ |\quad\ |\\ CONHC_6H_5\end{matrix}$.—This compound was prepared according to the directions of Bishop Tingle and A. Tingle,[1] from camphoroxalic acid and aniline, but instead of decomposing the resulting aniline phenylcamphoformeneaminecarboxylate with dilute hydrochloric acid, it was found to be more convenient to dissolve the salt in an aqueous solution of sodium carbonate and precipitate the acid by means of dilute hydrochloric acid. The yield is quantitative.

Action of Bromine on the Acid.—The bromine (4 atoms) was added gradually to phenylcamphoformeneaminecarboxylic acid, both substances being dissolved in dry chloroform. The solution was heated gently, hydrobromic acid was evolved immediately and white crystals soon deposited. These dissolve readily in alcohol or ethyl acetate, more sparingly in ether, acetone, or chloroform and they are insoluble in benzene. The purified material melts at 227–228°; it was identified as 3,4-dibromoaniline hydrobromide, $Br_2C_6H_3NH_2.HBr$.

Found: N, 4.30. Calculated: N, 4.22.

When mixed with water, the hydrobromide is dissociated into hydrobromic acid and 3,4-dibromoaniline, which crystallizes from the hot solvent in long needles, melting at 80–81°.

Found: C, 28 83; H, 2.07. Calculated: C, 28.46; H, 1.97

The compound was identified further by the preparation of the acetyl derivative, melting at 127°. This latter was obtained by heating the 3,4-dibromoaniline at 150°, during 30 minutes, with anhydrous sodium acetate and acetic anhydride. The substance (m. p. 216°) described by Bishop Tingle and A. Tingle[2] as being formed from bromine and phenylcamphoformeneamine,  $C_8H_{14}\!<\!\begin{matrix}C:CH\\ |\quad\ |\\ CONHC_6H_5\end{matrix}$, is, doubtless, 3,4-dibromoaniline hydrobromide.

The chloroform filtrate obtained after the separation of the 3,4-dibromoaniline hydrobromide, as described above, contains camphoroxalic acid, amounting, in some experiments, to 50 per cent. of the theoretical quantity. It was separated by evaporating the chloroform and extracting the tarry residue with an aqueous solution of potassium hydroxide. No unchanged phenylcamphoformeneaminecarboxylic acid could be detected.

Oxidation Experiments.—Phenylcamphoformeneaminecarboxylic acid does not appear to be attacked by chromic anhydride, at the ordinary temperature, during several days. Experiments were made in which acetone and also acetic anhydride were employed as solvents. With potassium permanganate, in moist acetone, a slow action takes place at the ordinary temperature. The permanganate solution was added gradually to the acid and the mixture allowed to remain during 24 hours, throughout which time the permanganate was in excess. During the evaporation of the acetone an odor of isocyanide was noticed; steam distillation of the tarry residue yielded camphorquinone, which was fully identified.

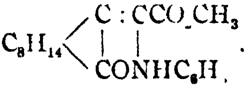
---

[1] *Am. Chem. J.*, **21**, 250.

[2] *Ibid.*, **21**, 248.

Action of Chlorides of Phosphorus on Phenylcamphoformeneaminecarboxylic Acid.—Phosphorus trichloride (2 mols.) and the acid were allowed to react at the ordinary temperature, during two days, in benzene which had been dried over sodium wire. After removal of the solvent a tarry material was obtained. It was extracted with an aqueous solution of sodium carbonate and then with one of potassium hydroxide. The undissolved residue was viscous and no crystals could be isolated from it. The alkaline solutions yielded camphoroxalic acid.

The action of phosphorus pentachloride appears to be exactly similar to that of the trichloride.

Action of Methyl Sulphate on Phenylcamphoformeneaminecarboxylic Acid.– The acid was dissolved in the calculated quantity of an aqueous solution of potassium hydroxide, and methyl sulphate (2.5 mols.) was added, while shaking, potassium hydroxide solution being run in at intervals so as to keep the mixture alkaline. An oil soon separates and after a time solidifies; it proved to be *methyl phenylcamphoformeneaminecarboxylate*,  $C_8H_{14}\left\langle\begin{matrix} C:CCO_2CH_3 \\ |\quad\;| \\ CONHC_6H_5 \end{matrix}\right.$. This ester dissolves without difficulty in acetone, ethyl alcohol, ethyl acetate, or benzene and is deposited from hot methyl alcohol, or ligroin in somewhat yellow crystals, melting at 127°.

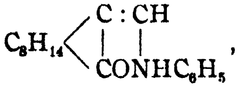
Found: C, 72.14; H, 7.23. Calculated: C, 72.84; H, 7.35.

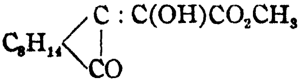
The ester is hydrolyzed rather slowly to the parent acid by boiling it with an aqueous solution of potassium hydroxide.

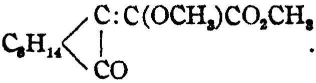
Methyl sulphate (1.1 mols.) reacts immediately, at the room temperature, with dry sodium phenylcamphoformeneaminecarboxylate (1 mol.) and sodium hydrogen carbonate (1 mol.). The product consists of the methyl ester described above; it was extracted by means of benzene.

A number of other experiments were carried out in which the conditions of temperature, etc., and of the relative proportions of acid and methyl sulphate were varied within somewhat wide limits, the object being to attack the NHC_6H_5 or the : COH group of the parent acid (see pp. 1500). In each case the only product which could be isolated was the ester described above.

A further effort in the same direction was made by heating at 140°, methyl phenylcamphoformeneaminecarboxylate (1 mol.) and dry potassium carbonate (1.5 mols.) and adding methyl sulphate (1.5 mols.). The mixture darkened immediately; ligroin extracted from it a quantity of unchanged methyl ester and left a black powder which melted above 270°.

No reaction appears to take place between phenylcamphoformeneamine,  $C_8H_{14}\left\langle\begin{array}{l} C:CH \\ | \quad\; | \\ CONHC_6H_5 \end{array}\right.$, and methyl sulphate, at 100°, in presence of dry sodium carbonate.

EXPERIMENTS WITH CAMPHOROXALIC ACID.—*Action of Methyl Sulphate.*—The acid was dissolved in a warm, aqueous solution of potassium hydroxide (1 mol.), and methyl sulphate and an aqueous solution of potassium hydroxide were added gradually and alternately, while shaking. An oil soon separates and finally solidifies. It consists of methyl camphoroxalate,  $C_8H_{14}\left\langle\begin{array}{l} C:C(OH)CO_2CH_3 \\ | \\ CO \end{array}\right.$.[1] The same product was also formed by heating dry sodium camphoroxalate, methyl sulphate and sodium hydrogen carbonate, in benzene, during one hour.

Methyl camphoroxalate, methyl sulphate and dry sodium carbonate, at 150–80°, gave a small quantity of an oil which was extracted by means of ether. The oil produced no coloration with alcohol and a solution of ferric chloride. It was treated with an alcoholic solution of potassium hydroxide, at the ordinary temperature, and the residue acidified. Ligroin extracted from the product an oil which gave a deep red coloration with ferric chloride and alcohol. These results indicate that the first oily material was *methyl methoxycamphoroxalate*,  $C_8H_{14}\left\langle\begin{array}{l} C:C(OCH_3)CO_2CH_3 \\ | \\ CO \end{array}\right.$.[2] Further experiments not only failed to improve the yield of this substance, but showed that its formation apparently depended on conditions which are rather difficult to duplicate, consequently the matter was not pursued further.

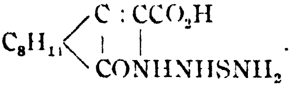
Nitrous acid, from sodium nitrite, or amyl nitrite, failed to react with phenylcamphoformeneaminecarboxylic acid, or with camphoroxalic acid and ethyl camphoroxalate. The experiments were made under varied conditions as to solvents and at temperatures ranging from —5° to that of the room.

Camphoroxalic Acid and Thiosemicarbazine.—The acid (2.25 g.) and the amine (0.91 g.) were mixed in alcoholic (95%) solution (30 cc.) and the liquid boiled in a reflux apparatus, during about 20 minutes, until a drop of it failed to give any color with ferric chloride. The reaction also proceeds slowly at the ordinary temperature, in presence of alcohol. A solution similar in concentration to that described above, gave a slight color with ferric chloride after 35 days, but no color was developed after 53 days. In benzene the reaction does not take place to any appreciable extent after 2 months at the ordinary temperature, but it proceeds slowly when heated on a boiling water bath. In all cases the product was viscous; it was purified by dissolving in a cold, aqueous solution of sodium carbonate, adding hydrochloric acid in excess and allowing the precipitate to remain over night in contact with the mother liquor. The solid material was then washed with water, dried and recrystallized from benzene. It is deposited in white flakes, melting at 148-9°. Analysis indicates that the substance is *thiosemicarbazylcamphoformeneamine-carboxylic acid*,

---

[1] *Am. Chem. J.*, 20, 334

[2] Cf. Bishop Tingle, THIS JOURNAL, 23, 390.



$$C_8H_{11}\left\langle\begin{array}{l} C : CCO_2H \\ \,|\quad\;\; | \\ CONHNHSNH_2 \end{array}\right..$$

Found: N, 14.16 Calculated: N, 14.14.

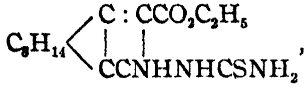
The yield is quantitative.

A study of the carboxylic acid shows that it exists in two modifications. The crystals (m. p. 148-9°) dissolve readily in a cold, aqueous solution of sodium carbonate. On adding dilute hydrochloric acid to this solution a sticky precipitate is deposited which is soluble in excess of the mineral acid. The precipitate hardens on standing and then melts at about 120-5°. This lower melting material dissolves readily in warm benzene, 100 cc. of which, at the boiling point, dissolve about 20 g. of the acid. After a short time crystals appear in the boiling liquid; these melt at 148-9° (the original melting point) and require more than 20 parts of boiling benzene for solution. The lower melting material (m. p. 120-5°) when heated on the water bath for a few hours, or if allowed to remain at the ordinary temperature during several days, shows a rise in melting point to 135-40° and a diminished solubility in benzene. A mixture of approximately equal quantities of the lower (m. p. 120-5°) and of the higher (m. p. 148-9°) melting varieties melts at 140-5°. The higher melting form dissolves readily in warm water and is deposited in the lower melting modification. Both forms are soluble without difficulty in ethyl acetate, acetone, alcohol (95%), ether and chloroform.

The carboxylic acid gives a slight greenish tint with alcohol and ferric chloride, the color disappears on adding ether. When a small crystal of the acid is placed on moist iron a red color is produced, doubtless due to the formation of a little ferric thiocyanate. No coloration was observed, under similar conditions, with metallic lead, zinc, or copper.

Fusion of the carboxylic acid leads to the production of resinous matter; in addition, a *compound* was formed which begins to melt at about 170°. Its quantity was too small to permit of its purification.

Ethyl thiosemicarbazylcamphoformeneaminecarboxylate,



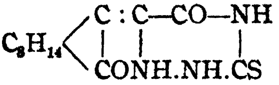
$$C_8H_{14}\left\langle\begin{array}{l} C:CCO_2C_2H_5 \\ |\quad | \\ CCNHNHCSNH_2 \end{array}\right.$$

, is prepared by dissolving the carboxylic acid in a small quantity of absolute alcohol and passing dry hydrogen chloride into the solution. The ester is deposited either by exposing the liquid to air, or by allowing it to remain overnight in a closed vessel. It forms white crystals from benzene and melts at 150–1°. Its distinction from the parent acid (m. p. 148–9°) was shown by a mixed melting point and also by the insolubility of the ester in an aqueous solution of sodium carbonate. In a warm aqueous solution of potassium hydroxide it dissolves slowly.

Found: C, 55.23; H, 7.18. Calculated: C, 55.38; H, 7.07.

Under certain conditions, which were not specifically determined, a small quantity of a white material is also formed together with the ester. It dissolves readily in cold water, melts above 300° and contains ionizable chlorine. Quite possibly it is ammonium chloride.

Action of Acetic Anhydride on Thiosemicarbazylcamphoformeneaminecarboxylic Acid.—The acid (1 g.) was heated on a boiling water bath, during 5 minutes, with acetic anhydride (5 cc.). A deep red solution was obtained, from which a resinous material separated when the liquid was poured into water (100 cc.). The solid was washed several times with water, then dried and recrystallized from glacial acetic acid; it is deposited in bright red crystals, melting at 181–2°. The compound is obtained in quantitative yield by dissolving the carboxylic acid in a little acetic anhydride and allowing the solution to remain at the room temperature until the anhydride and acetic acid have evaporated. This red compound is *thiosemicarbazylcamphoformeneaminecarboxylactimide,*

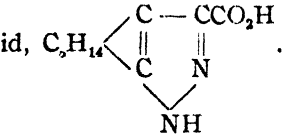


$$C_8H_{14}\left\langle\begin{array}{l} C:C\text{—}CO\text{—}NH \\ |\quad |\qquad\qquad | \\ CONH.NH.CS \end{array}\right.$$

; it dissolves readily in benzene, ligroin, alcohol, glacial acetic acid and also in a warm aqueous solution of potassium hydroxide; in a boiling aqueous solution of sodium carbonate dissolution takes place more slowly; when acidified each of these alkali solutions deposits the original carboxylic acid, m. p. 148–9°.

Found: C, 55.61; H, 6.14. Calculated: C, 55.91; H, 6.09.

Action of Acetic Anhydride and Concentrated Sulphuric Acid on Thiosemicarbazylcamphoformeneaminecarboxylic Acid.—The carboxylic acid (1 g.) was mixed with acetic anhydride (1.5 cc.), well shaken and concentrated sulphuric acid (3 drops) added. Heat is generated and a light brown solution is formed. After remaining during 15–20 minutes it was poured into water; a viscid solid is deposited which was washed with water, then with a dilute aqueous solution of sodium carbonate and finally purified by recrystallization from ethyl acetate. The crystals obtained in this manner melted at 261–2° and were shown, by analysis, by their properties and by a mixed melting point, to consist of camphylpyrazolecarboxylic acid,

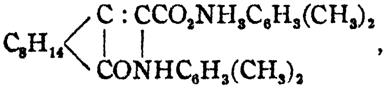


The material for comparison was prepared by a slight modification of the method of Bishop Tingle and Robinson.[1] Semicarbazylcamphoformeneaminecarboxylic acid was fused; the resulting product was finely divided and mixed with a cold, dilute aqueous solution of sodium hydrogen carbonate. The resinous material fails to dissolve, but the carboxylic acid slowly passes into solution and is reprecipitated by dilute hydrochloric acid.

The aqueous filtrate, obtained after the removal of the pyrazolecarboxylic acid which was prepared from the thiosemicarbazyl derivative, was tested with a ferric salt and was shown to contain thiocyanic acid.

Action of Concentrated Sulphuric Acid on Thiosemicarbazylcamphoformeneaminecarboxylic Acid.—A little of the carboxylic acid was ground to a paste with conc. sulphuric acid, and a solution, which was formed in the course of a few minutes, was allowed to remain during 3 days in an atmosphere dried by means of sulphuric acid. At the end of this period it was diluted with water; a precipitate was produced which consisted of unchanged carboxylic acid and a resin. From this no crystals could be separated.

Action of 1,3,4-Xylidine on Camphoroxalic Acid.—The acid (1 mol.) and the amine (2 mols.) were warmed together in benzene solution, during 10 minutes; after cooling, the liquid deposits a jelly-like material which was drained and dissolved in ligroin (b. p. below 90°). When the ligroin solution is allowed to evaporate moderately quickly, at the ordinary temperature, it deposits only a tarry substance, but if the liquid is placed in a small covered beaker and allowed to remain during 3 or 4 days, brown crystals of *1,3,4-xylidine 1,3,4-xylidylcamphoformeneaminecarboxylate*,

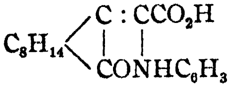


are deposited. The salt melts at 93–4° and dissolves readily in benzene, ligroin, acetone, ether, ethyl alcohol, chloroform, or ethyl acetate. An aqueous solution of potassium hydroxide decomposes the salt into an oil (1,3,4-xylidine) and the acid, which, however, is prepared more conveniently in the manner described below.

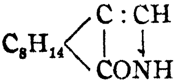
---

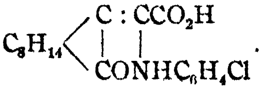
[1] *Am. Chem. J.*, 36, 259.

Found: N, 6.49. Calculated: N, 6.25 per cent.

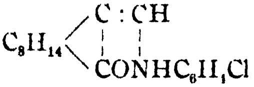
1,3,4-Xylidylcamphoformeneaminecarboxylic acid,  $C_8H_{14}\Big\langle\begin{matrix}C:CCO_2H\\ |\quad\ |\\ CONHC_6H_3(CH_3)_2\end{matrix}$, is obtained from the salt mentioned above, but is produced more readily by dissolving equimolecular proportions of camphoroxalic acid and 1,3,4-xylidine in benzene and warming the solution until a drop of it fails to produce a red color with alcohol and ferric chloride. The warming is continued while the liquid is well stirred with an aqueous solution of sodium carbonate; the two liquid layers are ultimately separated and the aqueous portion is acidified with dilute hydrochloric acid. The resulting sticky precipitate is purified by slow crystallization from low boiling ligroin. In this manner we obtained yellow crystals, melting at 117–8°. The acid dissolves readily in benzene, ligroin, ether, ethyl alcohol, acetone, chloroform, or ethyl acetate and also in an aqueous solution of sodium carbonate, from which mineral acids always precipitate it in a resinous condition. It gives no coloration with an alcoholic solution of ferric chloride.

Found: N, 4.41. Calculated: N, 4.28 per cent.

At 130°, a mixture of camphoroxalic acid and 1,3,4-xylidine evolves water and carbon dioxide; the product gave no coloration with an alcoholic solution of ferric chloride and it doubtless contained the compound  $C_8H_{14}\Big\langle\begin{matrix}C:CH\\ |\quad\ |\\ CONHC_6H_3(CH_3)_2\end{matrix}$, but no crystals could be isolated.

p-Chloroaniline and Camphoroxalic Acid.—When equimolecular proportions of these two substances are dissolved in benzene and heated during five minutes, crystals soon appear. They were purified by recrystallization from benzene, being deposited in yellow needles, melting at 182–3°. The compound consists of *p-chlorophenylcamphoformeneaminecarboxylic acid*,  $C_8H_{14}\Big\langle\begin{matrix}C:CCO_2H\\ |\quad\ |\\ CONHC_6H_4Cl\end{matrix}$. This acid, and not the *p*-chloroaniline salt, is also formed when camphoroxalic acid and *p*-chloroaniline are brought together in the ratio of 1 : 2 mols. The acid dissolves readily in benzene, ether, ethyl alcohol, acetone, or ethyl acetate. In ligroin the solubility is smaller. At the ordinary temperature, it dissolves easily in an aqueous solution of sodium carbonate and is reprecipitated by hydrochloric acid. The carboxylic acid gives no coloration with an alcoholic solution of ferric chloride.

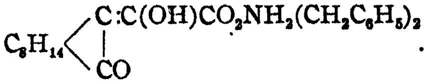
Found: N, 4.29. Calculated: N, 4.20 per cent.

Camphoroxalic acid and *p*-chloroaniline were ground together in equimolecular proportion and the mixture heated slowly by means of an oil-bath. At 65–70° the material melts; water is evolved at about 110° and the product then solidifies. It undoubtedly consists of the carboxylic acid, because it dissolves without difficulty, at the ordinary temperature, in an aqueous solution of sodium carbonate and it gives no coloration with an alcoholic solution of ferric chloride. As the heating is continued the material melts again at about 155° and evolves carbon dioxide. The temperature was maintained at 155–60° during 20 minutes, then allowed to fall to 110°, ligroin (b. p. 110–20°) was now poured onto the fused material and the mixture was shaken vigorously. Working in this manner, crystals were obtained immediately and were not seriously contaminated with resinous material. The compound consisted of *p-chlorophenylcamphoformeneamine*, 

$$C_8H_{14}\left\langle\begin{array}{l}C:CH\\ \vdots\quad\ \vdots\\ CONHC_6H_4Cl\end{array}\right.$$

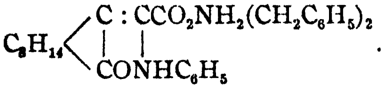
, it is deposited from acetone, on the addition of ligroin, in white crystals, melting at 194–5°. Yield, 61 per cent. of the calculated quantity. The compound dissolves readily in acetone, ether, ethyl acetate, alcohol, or chloroform, but it is less soluble in ligroin. It gives no coloration with an alcoholic solution of ferric chloride and is not changed by boiling with an aqueous solution of potassium hydroxide, or of hydrochloric acid. The same amine may also be obtained by heating *p*-chlorophenylcamphoformeneaminecarboxylic acid (see above), until carbon dioxide ceases to be evolved.

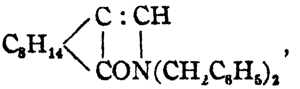
Found: N, 4.69 Calculated: N, 4.83 per cent

Dibenzylamine and Camphoroxalic Acid.—Equimolecular proportions of dibenzylamine and camphoroxalic acid were dissolved in benzene and heated during 15 minutes. After remaining, at the ordinary temperature during 2 hours, the liquid deposits a white, crystallin precipitate. It was washed with more benzene and dried and then melted at 135–6°. This melting point was lowered rather than raised by recrystallizing the substance. The same compound is obtained by the use of 2 molecular proportions of dibenzylamine. The compound dissolves readily in benzine, ethyl acetate, alcohol, acetone, ether, or chloroform. When warmed with dilute hydrochloric acid the substance is resolved into camphoroxalic acid and dibenzylamine and a similar decomposition is produced by an aqueous solution of sodium carbonate, slowly at the ordinary temperature, more rapidly when heated. The dibenzylamine produced in this way was identified by means of its hydrochloride. The analytical results given below show that the substance is formed by the direct addition of dibenzylamine to camphoroxalic acid, without the elimination of water. It gives a deep reddish purple coloration with an alcoholic solution of ferric chloride. These facts and the reactions described below lead us to regard the substance as *dibenzylamine camphoroxalate,*  $C_8H_{14}\left<\begin{array}{l} C{:}C(OH)CO_2NH_2(CH_2C_6H_5)_2 \\ | \\ CO \end{array}\right.$.

Found: N, 3.34. Calculated: N, 3.32 per cent.

The above dibenzylamine camphoroxalate was dissolved in benzene, aniline (2 mols.) added and the mixture heated at 100°, during 5 hours, in a sealed tube. After evaporation of the benzene, white crystals are deposited, they were washed with alcohol and, after being dried, melted at 185°.

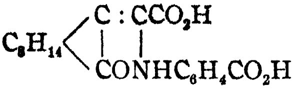
The compound dissolves very readily in benzene, more sparingly in alcohol. When treated with an aqueous solution of sodium carbonate it is resolved into dibenzylamine and phenylcamphoformeneaminecarboxylic acid (m. p. 172°). The amine was identified by the preparation of its hydrochloride (m. p. 256°) and the acid by a mixed melting point determination. These results show that the compound in question (m. p. 185°) is *dibenzylamine phenylcamphoformeneaminecarboxylate,*  $C_8H_{14}\left<\begin{array}{l} C:CCO_2NH_2(CH_2C_6H_5)_2 \\ |\quad | \\ CONHC_6H_5 \end{array}\right.$. The quantity of substance at our disposal was insufficient for an analysis.

A mixture of camphoroxalic acid and dibenzylamine, in equimolecular proportion, when heated, melts about 85°; it then becomes solid again and remelts about 125°. It was maintained at 135-40°, during 30 minutes. On cooling crystals are formed, they were washed with ligroin, and recrystallized from acetone. The compound melts at 152°; it is not changed by boiling with aqueous solutions of potassium hydroxide or of hydrochloric acid. Analysis shows that it is the dibenzylcamphoformeneamine,  $C_8H_{14}\left<\begin{array}{l} C:CH \\ |\quad | \\ CON(CH_2C_6H_5)_2 \end{array}\right.$, described by Bishop Tingle and Williams.[1] The yield is 75 per cent. of the calculated quantity. This substance is one of the most easily obtainable of its class and is well adapted for further study. The same amine is also formed by fusing either dibenzylamine camphoroxalate (see above), or a mixture of camphoroxalic acid (1 mol.) and dibenzylamine (2 mols.).

m-Aminobenzoic Acid and Camphoroxalic Acid.—Equimolecular alcoholic solutions of these substances were mixed and boiled during 5 minutes; after standing overnight a white solid separates, which is ultimately obtained in white crystals; melting at 136–7°; the melting point varies somewhat, according to the rapidity of the heating. The same compound is produced by the use of 2 molecular proportions of *m*-aminobenzoic acid. The substance consists of *m-carboxyphenylcamphoformene-*

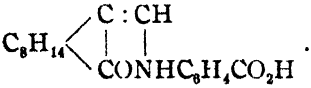
---

[1] *Am. Chem. J.*, 39, 117.

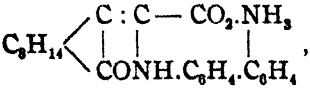
aminecarboxylic acid,  $C_8H_{14}\left\langle\begin{array}{l} C:CCO_2H \\ |\quad| \\ CONHC_6H_4CO_2H \end{array}\right.$; it dissolves readily in alcohol, ethyl acetate, or water, forming, in each case, a yellow solution. Rapid cooling, or quick evaporation of its solution causes the acid to be deposited in a gummy condition, but if the deposition takes place slowly crystals are produced. When dissolved in alcohol (95 per cent.) the acid gives no coloration with ferric chloride, but in water, or in 50 per cent. alcohol a portion of it is hydrolyzed to camphoroxalic acid, as is shown by its reaction with ferric chloride. A similar hydrolysis is produced by an aqueous solution of sodium carbonate, in which the dicarboxylic acid dissolves and liberates carbon dioxide; when acidified this solution reprecipitates the dicarboxylic acid in an impure condition.

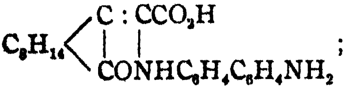
Found N, 4.37 Calculated. N, 4.08 per cent.

The above dicarboxylic acid evolves carbon dioxide when heated at its melting point; the residue is deposited from benzene in long, yellow needles, melting at 116–7°. It dissolves completely in a cold, aqueous solution of sodium carbonate, is reprecipitated by dilute hydrochloric acid and gives no coloration with an alcoholic solution of ferric chloride. These properties indicate that the compound is *m-carboxyphenylcamphoformeneamine,*


$C_8H_{14}\left\langle\begin{array}{l} C:CH \\ |\quad| \\ CONHC_6H_4CO_2H \end{array}\right.$.

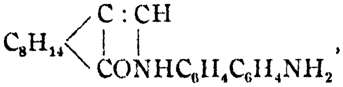
Benzidine and Camphoroxalic Acid.—When equimolecular benzene solutions of these substances are mixed and warmed for a short time, yellow crystals are soon deposited. After recrystallization, the compound melts at about 208°, depending somewhat on the rapidity with which the temperature is raised. The substance is only slightly soluble in alcohol, or ethyl acetate, it gives no color with an alcoholic solution of ferric chloride and dissolves only slowly in a boiling aqueous solution of potassium hydroxide, or of sodium carbonate. After remaining overnight, these clear alkaline solutions deposit a slimy material. If this is removed and the liquid acidified with hydrochloric acid the original compound is reprecipitated. Boiling, concentrated hydrochloric acid slowly hydrolyzes the compound to its constituents. Analysis shows that the substance is either an inner *ammonium salt,*


$C_8H_{14}\left\langle\begin{array}{l} C:C-CO_2.NH_3 \\ |\quad|\qquad\quad| \\ CONH.C_6H_4.C_6H_4 \end{array}\right.$, or *benzidylcamphoformeneaminecarboxylic acid,*


$C_8H_{14}\left\langle\begin{array}{l} C:CCO_2H \\ |\quad| \\ CONHC_6H_4C_6H_4NH_2 \end{array}\right.$; its behavior towards alkalies is, we think, in better accord with the salt formula.

Found: N, 6.98. Calculated: N, 7.18 per cent.

The melting point (208°) which we observed for the above compound is 18° higher than that recorded by Bishop Tingle and Hoffman[1] for a substance which they obtained from benzidine and camphoroxalic acid, in alcoholic solution. A repetition of their work shows that the two compounds are identical, except for the fact that ours is more nearly pure. A mixture of the two substances melts at the same temperature as either one alone. The difference in the melting point is due partly to this greater degree of purity and partly to the rather large variation which is produced in the melting, or more accurately, the decomposing point, by a difference in the rate at which the temperature is caused to rise. That some of the compounds of this series are extremely sensitive in this respect has been pointed out previously by Bishop Tingle and Robinson.[2]

Benzidylcamphoformeneamine, 
$C_8H_{14}\left<\begin{array}{l}C:CH\\ |\quad\ |\\ CONHC_6H_4C_6H_4NH_2\end{array}\right.$, is formed by direct fusion of the preceding compound, but is best prepared by grinding a quantity of it with 5 parts of nitrobenzene, the mixture being then slowly heated on an oil bath. At about 135° a clear red solution is obtained; at 150° water and carbon dioxide are evolved. The temperature was maintained at 150-5° during 15 minutes and the solution then filtered and allowed to cool. The crystals which separated were collected, washed with benzene by means of a centrifuge and, finally, they were boiled with alcoholic potassium hydroxide. The purified material melts at 317-8°, it is not attacked by boiling with concentrated aqueous solutions of potassium hydroxide, or of hydrochloric acid. The analytical results given below and the method by which the compound is formed can leave no doubt as to its nature, but concordant data could not be obtained for its nitrogen content; the gas is evolved very slowly during the course of the combustion and some of it is evidently occluded in the filling material of the combustion tube. See K. Holdermann and R. Scholl.[3]

Found: C, 79.00; H, 7.79. Calculated: C, 79.77; H, 7.54.

Camphylamine and Camphoroxalic Acid.—A well-marked evolution of heat takes place when these substances are mixed, in benzene solution; the residue, obtained after evaporating the solvent, is evidently a condensation product, because it fails to give any coloration with an alcoholic solution of ferric chloride, but we were unable to obtain the substance in a crystallin condition. When camphoroxalic acid is heated at 150-5°, with 2 molecular proportions of camphylamine, most of the product is also tarry, but a while, crystalline *sublimate* is obtained in small quantity. It melts at 105°, dissolves readily in alcohol and also in an aqueous solution of sodium carbonate, at the ordinary temperature. It gives no coloration with an alcoholic solution of ferric chloride.

---

[1] *Am. Chem. J.*, **34**, 231, 250.

[2] *Ibid.*, **36**, 229

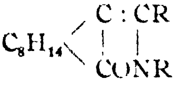
[3] *Ber.*, **43**, 342

No definite compound could be isolated from the reaction products of *p*-aminobenzaldehyde and camphoroxalic acid, at 125–30°.

Some further experiments which have been made with acetylphenylhydrazine and camphoroxalic acid have failed to improve the yield of the condensation compound described by Bishop Tingle and Williams.[1]

Summary.

(1) We have studied the action of bromine, of the chlorides of phosphorus, of various oxidizing agents, of nitrous acid and of dimethyl sulphate on certain of the condensation compounds of camphoroxalic acid and amines, in order to obtain further data in respect to their constitution.

(2) The results which we have obtained are in accord with the formula,  $C_8H_{14}\left\langle\begin{array}{l} C:CR \\ \;|\quad| \\ CONR_1R_2 \end{array}\right.$, ($R = H$ or CO_2H; R_1 and $R_2 = H$, alkyl or aryl), which has been previously assigned to these condensation compounds by the senior author and his colleagues.

(3) The interaction of thiosemicarbazine and camphoroxalic acid has been studied in order to compare the resulting compounds with those derived from semicarbazine. The replacement of CO (semicarbazine) by CS (thiosemicarbazine) greatly reduces the tendency of the primary condensation compounds to form cyclic derivatives.

(4) A considerable number of new condensation compounds have been prepared from camphoroxalic acid and the following amines: *1,3,4-xylidine, p-chloroaniline, dibenzylamine, m-aminobenzoic acid, benzidine* and *camphylamine*. Some of these new substances are well adapted for further study. No crystalline compound could be obtained from camphoroxalic acid and *p*-aminobenzaldehyde.

The investigation will be continued in various directions.

McMaster University, Toronto, Canada

THE DEVIATION OF FERMENT ACTION FROM THE MONOMOLECULAR LAW WITH ESPECIAL REFERENCE TO THE ESTERASES.

By George Peirce.

Received July 28, 1910.

During the course of an investigation into the effect of the fluorides on the action of lipase, it became necessary to study the kinetics of the lipolytic action. The results obtained were so unexpected that it seemed worth while to publish them separately.

---

[1] *Am. Chem. J.*, 39, 120.

The reaction

$$\text{Ester} + \text{Water} \rightleftarrows \text{Acid} + \text{Alcohol}$$

is in its most general form a reaction of the second order, since we have two substances changing their concentrations in each semi-reaction. As usually studied, the water is present in large excess and may therefore be regarded as constant.

The semi-reaction

$$\text{Ester} + \text{Water}$$

should then be written

$$\text{Ester} + \text{Water (in excess)} \longrightarrow$$

and the whole reaction takes the form

$$\text{Ester} + \text{Water (in excess)} \rightleftarrows \text{Acid} + \text{Alcohol} + \text{Water (in excess)}.$$

Thus on the left side we have only one substance, the ester, changing its concentration, while on the right side we have two, the acid and the alcohol. Under these conditions, the reaction from left to right is better studied as a reaction of the first order. For such reactions we expect the following equation to hold:

$$\frac{1}{t} \log \frac{a}{a - x} = k.$$

Here k is a constant, a is the amount of ester present at the beginning of the reaction and x the amount of ester split up during the time t. In the following experiments a and x are measured in terms of 0.05 N NaOH.

The reaction from right to left has been studied qualitatively in several researches but so far as I know Bodenstein and Dietz[1] have been the only ones to investigate its kinetics. We will consider, therefore, in this discussion only the reaction from left to right or the hydrolytic reaction.

The researches fall into two divisions, reactions in homogeneous and reactions in heterogeneous solutions. We will consider briefly examples of each class and take up first the reaction in homogeneous solutions.

Kastle and Loevenhart[2] and later Kastle, Johnston and Elvove,[3] using a clear liver extract and ethyl butyrate found that when an attempt was made to calculate their results according to the first-order equation $k = 1/t \log [a/(a - x)]$, k fell off steadily from the beginning to the end of the reaction. They attributed this fact to the inhibiting influence of the acid on the enzyme. Towards the end of Kastle Johnston and Elvove's paper, however, occurs a series of experiments where the function falls off only very slightly. In this series, moreover, the value of *k*, though nearly constant for any given concentration of ethyl butyrate, is, roughly speaking, inversely proportional to the initial concentration of the esterase, when this is varied. Thus though the monomolecular law is closely followed in one concentration of zymolyte, the reaction taken as a whole is at total variance with the law.

---

[1] Bodenstein and Dietz, *Z. Elektrochem.*, 12, 605 (1906); Dietz, *Z. physiol. Chem.*, 52, 279 (1907).

[2] Kastle and Loevenhart, *Am. Chem. J.*, 24, 491 (1900).

[3] Kastle, Johnston and Elvove, *Ibid.*, 31, 521 (1904).

Euler[1] also obtained a constant value for *k*, using a clear esterase prepared from pig's adipose tissue and ethyl butyrate. As he gives only one experiment and did not vary the concentration of the butyrate, it is impossible to say that the monomolecular law is obeyed.

Turning now to the reaction in heterogeneous solution, we will consider first the lipase from the castor oil bean (*Ricinus communis*). Armstrong and Ormerod[2] have shown that a slightly acid medium is necessary for the action of this enzyme, but that variations of 2500 per cent. in added acetic acid and of 500 per cent. in added citric acid make practically no difference in its hydrolysis of castor oil. Although this lipase has unfortunately been obtained only in insoluble form it should on account of its behavior towards acids be of great value for kinetic work. Animal lipases act best in a nearly neutral medium and apparently do not act on such a wide variety of esters as the ricinus lipase. The nature of the two lipases therefore may be fundamentally different. A. E. Taylor[3] in his work on this ferment found that in one instance it showed complete agreement with the monomolecular law. Working under rather difficult experimental conditions, he found that the values of *k* agreed very closely when triacetin was used as zymolyte. The extreme variation in each series was about 25 per cent., but for three different concentrations of ester, 0.5 per cent., 1 per cent. and 2 per cent., the mean values of *k* agreed very closely. When, however, he used ethyl acetate he found that *k* was about twice as great in the 2 per cent. as in the 1 per cent. solution. The result with triacetin is, of course, of the greatest importance. The result with ethyl acetate is practically unique, as in all other cases of enzyme action that are comparable with this *k* is greater in the weaker concentrations of the zymolyte. I cannot, however, pretend to have consulted more than a small part of the literature.

Very interesting and significant results have also been obtained by Bodenstein and Dietz,[4] using a turbid pancreatic extract and amyl butyrate They followed the reaction in both directions and obtained good agreement with the *mono*- and *bi*-molecular laws as long as they did not vary the initial concentration of their zymolyte. When this was varied, however, they, too, found that k likewise varied in inverse proportion.

---

[1] Euler, *Beitr. Chem. Physiol.* (*Hofmeister*), 7, 1 (1905). Experiment referred to is on pages 13 and 14.

[2] Armstrong and Ormerod, *Proc. Royal. Soc.*, 78, 376 (1906).

[3] Taylor, *J. Biol. Chem.*, 2, 87 (1905).

[4] Bodenstein and Dietz, *Z. Elektrochem.*, 12, 605 (1906), Dietz, *Z. physiol. Chem.*, 52, 279 (1907).

A great variety of other results have been obtained but the few researches given above are typical of the more careful work done during the past ten years. The investigators who consider that they have confirmed Schütz's rule (to be considered in the next paragraph) have for the most part worked with heterogeneous systems of at least three phases. This makes their work extremely difficult to interpret. It is noteworthy that practically everyone who has worked with the simpler solutions considers that Schütz's rule is, in the case of lipase at least, untenable, and that the amount of enzyme action is proportional to the mass of the enzyme. These results are scattered through the literature but some experimental evidence for the statement will be given later.

It may not be out of place in this connection to consider Schutz's rule. It may be given as follows: With a given reaction volume and a given initial concentration of zymolyte the amount of reaction products are proportional to the product of the square root of the enzyme mass and the square root of the time. Expressed in a formula this may be written $x = k\sqrt{Et}$ where x = the amount of reaction products, k = a constant for the stated volume and zymolyte concentration, E = the enzyme mass and t = the time.

Generally speaking, we cannot consider it improbable that the zymolyte and its reaction products will influence the activity of the enzyme and will do so differently in their different concentrations. Therefore it is better to compare the strength of the enzyme in two different solutions by the time taken to attain to a given stage of the reaction. In this way we shall eliminate as far as possible the different activity of the enzyme in different conditions of the medium. Working on this principle we can measure the activity of the enzyme by the reciprocal of the time taken to produce a given quantity of reaction products. (The reaction volume and initial zymolyte concentration are, of course, supposed to be constant.) For instance, if in one reaction mixture it takes twice as long to produce a given amount of acid as in another reaction mixture, we may say that the first reaction mixture has twice the enzymic activity of the second. We may formulate this by saying that Enzymic activity = k/t or Enzymic activity $\times\ t = k$; where k is a constant for given initial conditions (with exception of enzymic mass) and given amount of reaction products. This is a general rule in the nature of a definition, and therefore independent of all experimental evidence.

If, however, in addition, we find that the enzymic activity as determined in this way is proportional to the enzymic mass, we will have a most valuable experimental rule. We may formulate it $Et = k$, where E = the enzyme mass (an experimentally given quantity). As we have stated, this rule is of the greatest empirical value besides having abundant theoretical justification. Schütz's rule, on the other hand, requires a rather elaborate theoretical calculation to justify its existence and as the experimental work becomes more carefully planned is seen to have less and less empirical value.

Thus as a summary of the above researches we may say that the lipolytic reaction has frequently been shown to follow the monomolecular law so long as only one initial concentration of zymolyte was employed. In only one case (triacetin and ricinus lipase) was k shown to be the same with different concentrations of zymolyte. In another case k and the initial concentration of the zymolyte were directly proportional to each other. In all other cases k was larger in the weaker zymolyte concentrations, in some cases being inversely proportional to the concentration. The amount of enzymic action as measured by the reciprocal of the time to attain a given stage of the reaction was proportional to the mass of enzyme present.

In my investigation I have used a carefully dried and twice redistilled ethyl butyrate and the lipase prepared from pig's liver. The enzyme solution was prepared as follows: Small pieces of freshly killed pig's liver were dissected free from vessels and connective tissue and rinsed off with distilled water. These pieces were then ground with sand and water and strained through cloth. The extract obtained from 50 cc. of liver was made up to 500 cc. and the resulting solution called "10 per cent." extract. After several days' standing under toluene at room temperature this was filtered through paper and a clear, highly refractive, deep straw-colored liquid obtained. It was again filtered after two and again after nine months. The filtrate was now much lighter than formerly, though still quite active, and was much more suitable for use with indicators. A small portion of this solution was mixed with 500 cc. of an ethyl butyrate solution previously warmed to 37° and the mixture kept at this temperature The time of the beginning of the reaction (which was not more than 3 seconds in error) was taken as the time when one-half of the enzyme had flowed into the ethyl butyrate solution from a pipette. At suitable intervals 50 cc. of this solution was removed with a pipette, allowed to flow onto snow in a beaker and immediately titrated with 0.05 N NaOH free from carbonate, phenolphthalein being used as an indicator. The time of completion of the reaction was taken when one-half of the solution had gone onto the snow. The error in the measurement of t was probably not more than 6 seconds and the error in the measurement of x not more than 0.10 cc. though generally less than 0.5 cc. In all cases the acidity of the extract used has been deducted from the observed figures, so that the figures given are all corrected ones. For each 50 cc. of reaction mixture the initial acidity was 0.82 cc. 0.05 N

NaOH in the 0.476 per cent. solution, 0.34 cc. in the 0.196 per cent. solution and 0.17 cc. in the 0.099 per cent. solution.

The largest error is undoubtedly the temperature error. The temperature of the bath was within 0.1° of 37° during practically the entire reaction, but occasionally varied 0.2–0.4° for a few minutes. As the temperature coefficient of the reaction is about 10 per cent. for each degree, this introduces a slight factor of uncertainty, but it was not possible under my limitations of time to secure a better regulation, nor would the results to have been attained have warranted it. All experiments were done in duplicate, except the experiment in the 4th column in Table VII. As it differs slightly from the others, however, I did not feel justified in excluding it absolutely.

After considerable preliminary work in perfecting the technique, my first experiment showed that the reaction velocity fell off gradually from the beginning of the reaction.

TABLE I.

Enzyme 0.476%[1] $a = 42.77$.

x in cc. 0.05 N NaOH.	t in min	$1/t \log [a/(a-x)]$.
8.78	22.83	0.004371
8.71	22.83	0.004332
13.76	41.00	0.004112
13.13	40.33	0.003949
17.61	61.67	0.003736
17.70	62.33	0.003722
22.56	91.50	0.003558
22.56	93.33	0.003488
26.11	121.00	0.003383
25.88	121.33	0.003326
31.37	186.33	0.003082
31.53	187.08	0.003102
34.03	235.17	0.002932
34.01	234.50	0.002937
36.63	320.25	0.002632
36.88	321.33	0.002680
37.84	367.25	0.002555
37.68	366.58	0.002522
39.54	487.5	0.002301
39.43	488.0	0.002269

This falling off was supposed to be due to the accumulation of acid in the system, in accordance with the explanation proposed by Kastle, Johnston and Elvove. To test this hypothesis further, I used a much more dilute solution of enzyme (0.099 per cent.), so that the reaction would be better followed, and also used six different strengths of zymolyte.

---

[1] 25 cc. "10 per cent." liver extract + 500 cc. ethyl butyrate solution.

TABLE II.

Enzyme 0.099%.

$a = 43.53$			$a = 32.56$		
x.	t.	$1/t \log [a/(a-x)]$	x.	t.	$1/t \log [a/(a-x)]$.
1.07	9.63	0.001123	1.02	9.17	0.001507
1.14	10.03	0.001150	1.00	8.75	0.001548
1.95	18.88	0.001055	1.94	19.12	0.001395
2.00	19.95	0.001024	2.05	19.85	0.001423
2.81	30.00	0.000966	2.94	30.62	0.001342
2.94	31.33	0.000969	...	.. ..	....
3.91	44.83	0.000912	3.80	42.53	0.001267
3.97	45.05	0.000922	3.98	45.27	0.001251
4.86	59.13	0.000870	5.23	62.95	0.001208
4.96	59.42	0.000884	5.20	62.43	0.001210
6.15	78.47	0.000843	6.16	77.23	0.001179
6.35	79.90	0.000857	6.26	78.47	0.001182
7.17	96.00	0.000814	7.08	91.10	0.001169
7.32	96.70	0.000827	7.07	91.25	0.001165
7.97	110.00	0.000798	7.96	106.03	0.001148
8.11	110.75	0.000808	8.12	108.40	0.001149
8.94	127.88	0.000781	9.04	124.62	0.001133
9.22	130.58	0.000792	9.05	124.60	0.001135
9.97	148.30	0.000762	9.93	141.62	0.001116
10.16	149.17	0.000774	9.97	142.63	0.001113

$a = 21.40$			$a = 10.62$		
x.	t.	$1/t \log [a/(a-x)]$.	x.	t.	$1/t \log [a/(a-x)]$.
1.26	11.45	0.002301	1.06	9.77	0.004675
1.21	10.82	0.002335	1.03	9.45	0.004689
2.21	21.75	0.002176	2.01	20.20	0.004511
2.26	22.07	0.002196	2.04	20.08	0.004614
3.19	33.37	0.002101	3.22	34.42	0.004558
3.25	33.73	0.002121	3.12	33.58	0.004497
4.04	43.62	0.002082	4.18	47.17	0.004577
4.01	43.53	0.002070	4.18	47.58	0.004538
4.94	55.75	0.002045	5.23	61.33	0.004802
4.98	56.07	0.002051	5.00	60.37	0.004578
6.02	70.47	0.002035	5.96	74.75	0.004785
6.02	70.65	0.002030	5.99	75.95	0.004747
7.03	85.63	0.002019	6.92	93.80	0.004882
7.16	87.57	0.002020	6.92	94.83	0.004829
8.13	103.62	0.002002	7.93	119.33	0.004997
8.09	102.87	0.002004	7.97	121.33	0.004969
9.10	121.00	0.001988	8.78	151.50	0.005025
9.20	121.75	0.002004	8.74	153.25	0.004906
10.11	140.58	0.001975	9.68	212.50	0.004955
10.19	140.12	0.002004	9.74	216.45	0.004998

TABLE II (*Continued*).

Enzyme = 0.099%.

$a = 5.66$			$a = 2.74$		
x.	t	$1/t \log [a/(a-x)]$	x.	t.	$1/t \log [a/(a-x)]$.
0.62	5.72	0.00881	0.64	5.65	0.0205
0.59	5.73	0.00834	0.60	5.38	0.0200
1.32	14.47	0.00797	1.10	13.15	0.0170
1.31	14.42	0.00793	1.02	11.97	0.0169
1.87	21.68	0.00804	1.70	21.07	0.0200
1.89	21.83	0.00809	1.66	21.98	0.0184
2.46	30.05	0.00824	2.06	31.23	0.0194
2.44	30.08	0.00814	2.14	32.88	0.0201
3.24A	43.05	0.00857	2.41	47.90	0.0192
3.47A	47.12	0.00875	2.44	52.88	0.0182
3.87	55.88	0.00895	2.57	77.32	0.0156
3.88	56.75	0.00885	2.53	78.05	0.0143
4.31	67.35	0.00924	..	...	....
4.30	67.67	0.00915		....	....
4.70	81.75	0.00943	....	...	...
4.76	83.43	0.00957	.	...	...
5.03	99.80	0.00954	...	..	.
5.04	101.17	0.00949	..	..	.....
5.26B	134.8	0.00854		.	...
5.38B	156.5	0.00834		...	..

The two observations marked A were taken from the first reaction mixture and those marked B from the second.

TABLE IIa.

Values of $1/t \log [a/(a - x)]$ for different values of x.

Enzyme = 0.099%

x.	$a = 43.53$	$a = 32.56$	$a = 21.40$	$a = 10.62$	$a = 5.66$	$a = 2.74$
1.00	0.001149	0.001529	0.002350	0.004688	0.00795*	0.00170*
2.00	0.001038	0.001409	0.002211	0.004565	0.00810	0.00198*
3.00	0.000960	0.001337	0.002125	0.004528*	0.00843	......
4.00	0.000914	0.001253	0.002077	0.004543	0.00896	.....
5.00	0.000874	0.001217	0.002047	0.004683	0.00952*	....
6.00	0.000856	0.001191	0.002033	0.004768		....
7.00	0.000828	0.001169	0.002021	0.004865	.	....
8.00	0.000804	0.001150	0.002004	0.004983*	...	....
9.00	0.000788	0.001135	0.001997	0.004966	.....	....
10.00	0.000769	0.001114	0.001991	0.004977	.....	....

These figures are obtained by interpolation and occasional extrapolation from Table II. The function changes slowly for any given series and the calculation therefore is generally not difficult. Whenever the observed figures show a maximum or minimum I have used that maximum or minimum value for the nearest corresponding value of x, as it would probably lie nearer the true value than a figure obtained by interpolation. The six cases where this occurs are marked in the table by an asterisk (*).

I naturally expected that "k" would be the same in each concentration or very nearly so and that it would show a falling off from the beginning to the end of the reaction. Instead of this it was, roughly speaking, inversely proportional to the concentration of the ester.[1] Further, the function $1/t \log [a/(a - x)]$, though falling off markedly in the two stronger solutions, fell off only slightly in the "$a = 21.40$" solution, and even increased in the other three.

If we tabulate the time taken to split a definite amount of ethyl butyrate, the apparent law becomes clearly evident. We find that this time is practically independent of the concentration of the butyrate itself, whereas by the mass law it should bear an inverse relation to it. The time taken to split up a given amount of ethyl butyrate first shows perceptible increase when the concentration of the ester falls below $N/200$ (*i. e.*, 5.00 cc. of 0.05 N NaOH per 50 cc.). These times are given in Table III. The figures are obtained by calculating backward from the values of $1/t \log [a/(a - x)]$ given in Table II*a*.

TABLE III.

Time in minutes to produce x cc. of acid.

Enzyme — 0.090%

x	$a = 43.53$	$a = 32.56$	$a = 21.40$	$a = 10.62$	$a = 5.66$	$a = 2.74$.
0.60	.	.	.	.	5.66	5.29
1.00	8.78	8.85	8.84	9.16	10.62	11.61
1.50	. .	.	.	. . .	16.82	18.42
2.00	19.68	19.54	19.27	20.07	23.37	28.72
2.43		.	. .	. . .	29.78	50.61
3.00	32.30	31.40	30.87	31.82	38.90	. . . .
4.00	45.80	45.43	43.26	45.17	59.45	. . . . .
5.00	60.83	59.49	56.46	59.02	98.0	. . . .
6.00	75.25	74.27	70.29	75.78	133.0	. . .
7.00	91.96	89.92	85.13	96.08		. . .
8.00	109.69	106.48	101.45	121.98	.	. .
9.00	127.65	123.79	118.67	164.44	. .	. . .
10.00	147.41	143.03	137.37	249.49	. .	. .

The table is divided into three parts by two broken lines. To the left of the heavy line where the ester concentrations is above $N/200$, the figures on each horizontal line are nearly the same (*i. e.*, within 8 per cent. of each other). To the right of the dotted line they are con-

---

[1] This statement is true only for the values corresponding to $x = 1.00$ but anyone who cares to do so can see that it is also nearly true for other values of x, if the expression

$$\frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$$

is used. Table III can be used as a basis for this calculation.

siderably larger. Between the heavy and the dotted lines they are only slightly larger (10–15 per cent.) than the figures to the left of the heavy line.

It will be noticed that it took longer to produce 10 cc. of acid in the $a = 43.53$ solution than in the $a = 32.56$ or $a = 21.40$ solutions. Whether much importance should be attributed to this fact I cannot say. It seems to be a greater difference than can be accounted for by experimental errors.

The facts brought out in Table III can be shown even more plainly if instead of the time taken to produce x cc. of acid we tabulate the time taken to produce 1 cc. of acid at different stages of the reaction. Thus the time taken to produce the first cc. of acid in the three stronger solutions is 8.78, 8.85 and 8.84 minutes, respectively, while the time taken to produce the second cc. is 10.90, 10.69 and 10.43 minutes.

TABLE IV.

Time in minutes to produce 1 cc. of acid in different acid concentrations.

Concentration of acid	Enzyme = 0.099 per cent.					
	$a = 43.53$	$a = 32.56$	$a = 21.40$	$a = 10.62$	$a = 5.06$	$a = 2.74$
$x = 0.00–1.00$	8.78	8.85	8.84	9.16	10.62	11.61
$x = 1.00–2.00$	10.90	10.69	10.43	10.91	12.75	17.11
$x = 2.00–3.00$	12.62	11.86	11.60	11.75	15.53	....
$x = 3.00–4.00$	13.50	14.03	12.39	13.35	20.55	
$x = 4.00–5.00$	14.83	14.06	13.20	13.85	38.55	...
$x = 5.00–6.00$	14.61	14.78	13.83	16.76	.	.....
$x = 6.00–7.00$	16.71*	15.65	14.84*	20.30	..	.....
$x = 7.00–8.00$	17.73	16.56	16.32	25.90	.....	.....
$x = 8.00–9.00$	17.96	17.31	17.22	42.76	....	.....
$x = 9.00–10.00$	19.76	19.24	18.70	85.05	.....	....

* These two asterisks note the largest deviation to the left of the heavy line.

Here we notice the important fact that the time taken to produce 1 cc. of acid depends mainly on the reaction of the medium and very little on the concentration of the ethyl butyrate. That is, as long as the concentration of the ester is above $N/200$ it takes practically the same time to produce 1 cc. of acid in a mixture of given acidity. Although above this limit the concentration of the ester makes very little difference, yet when it falls below this limit the time taken to produce 1 cc. of acid increases rapidly. This is seen very well by comparing the 3rd and 4th series in the above table. In contrast to this comparative independence of the ester concentrations, the reaction of the medium is of the greatest importance. For instance, in the three stronger solutions it takes about twice as long to produce the ninth cc. of acid as the first cc. In the $a = 21.40$ solution the ester concentration has by this time fallen to about five-eighths its original value. It therefore makes little difference in this one case whether we attribute this increase in time to the diminished ester concentration or the increased acidity. In the two stronger solutions, however, the ester concentration has fallen only to $^3/_4$ and $^4/_5$ of its initial value and we should therefore expect it to take only $^4/_3$ and $^5/_4$ as long to produce the ninth cc. of acid as the first. Instead we find that in these two solutions, as well, the time is approximately doubled. If we assume that the reaction would have followed the monomolecular law, but that the activity of the enzyme is decreased by the acidity of the solution, we see from Table II*a* that it is diminished in different amounts in these three solutions, and is actually increased in the $a = 10.62$ solution.

We see, therefore, from this series of experiments, that on its face, at least, the reaction does not follow the monomolecular law. Even when only one reaction at a time is considered, the explanation required is complicated, while when the six series are considered together the difficulties become almost insuperable. The amount of material reacting per instant is not proportional to the amount of material present at that instant, even when due allowance is made for acidity. On the other hand, provided only that the acidity is the same in the two solutions to be compared, the amount of ester reacting per instant is practically independent of the ester concentration over considerable wide limits ($N/23$–$N/200$).

We may indeed well question whether the constancy of the function $1/t \log [a/(a - x)]$ for the two series $a = 10.62$ and $a = 21.40$ is not purely accidental.

The question then arises: how are we to explain this apparent deviation from the mass law? The answer is, I think, very simple. We may assume that the action takes place in two stages with the formation of an intermediate compound. The first stage is a reaction between the enzyme and the zymolyte (here the ethyl butyrate) with the formation of this hypothetical intermediate compound; the second stage is the splitting up of this intermediate substance into free enzyme, alcohol and acid. At what stage of the reaction the water enters into this series of changes is not important for the following discussion, but we can represent the possibilities in two ways.

In the first equation the water does not enter into the formation of the intermediate compound, while it does in the second equation.

$$\text{Ester} + \text{Enzyme} + \text{Water} \rightleftarrows \left(\begin{smallmatrix}\text{Ester}\\ \text{Enzyme}\end{smallmatrix}\right) + \text{Water} \rightleftarrows \text{Alcohol} + \text{Acid} + \text{Enzyme}$$

or

$$\text{Ester} + \text{Enzyme} + \text{Water} \rightleftarrows \left(\begin{smallmatrix}\text{Ester}\\ \text{Enzyme}\\ \text{Water}\end{smallmatrix}\right) \rightleftarrows \text{Alcohol} + \text{Acid} + \text{Enzyme}.$$

By the mass law, the amount of acid production (which is what we measure) would be proportional to the concentration of this intermediate compound. If then our reaction constants bear such a proportion to each other that in ester concentrations from $N/23$ to $N/200$ most of the enzyme is held in such a compound, we can easily see that the amount of hydrolysis would be practically independent of our ester concentration.

With a little further consideration we can even make an approximate calculation of the percentage of enzyme present in the free and combined states. In the first place the amount of enzyme is so small that the total quantity present must react several times per second, and hence the system can never be very far from equilibrium so far as the enzyme itself is concerned. This being so, we have:

$$(\text{Concentration free enzyme})^m \times (\text{Concentration ester})^n = k_1\,(\text{Conc. intermediate compound})^p$$

where m, n and p represent the number of molecules of the substances entering into the reaction.

We have, however, absolutely no data for assigning values to m, n and p and hence can simplify the equation by making them equal to 1, that is by assuming that one molecule of enzyme reacts with one molecule of ester to form one molecule of the intermediate compound.

We have then:

$$\text{Conc. free enzyme} \times \text{Conc. ester} = k_1\ \text{Conc. int. compd.} \qquad (1)$$

and since the amount of acid produced per instant (or per small unit of time[1]) is proportional to the concentration of our intermediate compound we have:

$$k_2\ \text{Conc. int. compd.} = \text{acid produced per minute} \qquad (2)$$

from which we can obtain by division a third equation:

$$\text{Conc. free enz.} \times \text{Conc. ester} = k_1/k_2\ \text{acid produced per minute.} \qquad (3)$$

Using these equations as a basis for calculation I obtained the figures in the following table (Table V). The mean amount of ester present during the production of the first cc. of acid is the acid equivalent of the ester present at the beginning of the reaction minus 0.5 cc The rate of acid production is also a mean value, being merely the reciprocal of the time taken to produce the first cc. of acid.

TABLE V

	Enzyme = 0.009%.					
	a = 43.53.	a = 32.56	a = 21.40	a = 10.62.	a = 5.66	a = 2.74.
Mean concentration of ester during production of 1st cc. of acid	43.0	32.1	20.9	10.1	5.16	2.24
Minutes taken to produce 1 cc. of acid	8.78	8.85	8.84	9.16	10.62	11.61
cc. of acid produced per minute	0.114	0.113	0.113	0.109	0.094	0.086
Free enzyme (per cent. of total enzyme)	1.7	2.3	3.7	7	12	25
Combined enzyme (per cent. of total enzyme)	98.3	97.7	96.3	93	88	75

---

[1] To avoid the difficulties of the differential notation, I have generally used a small but finite time and quantity unit (1 minute and 1 cc.). The error is, I think, very small.

The figures in the last two lines are obtained by successive approximations and it would not be of especial interest to give these at length. Instead I give a table which shows that they coincide very nearly with the observations.

TABLE VI.

	Enzyme = 0.099%.					
	$a = 43.53$	$a = 32.56$.	$a = 21.40$.	$a = 10.62$	$a = 5.66$	$a = 2.74$.
$\frac{\text{Acid produced per minute}}{\text{\% free enzyme} \times \text{mean amt of ester}}$	0.0153	0.0153	0.0150	0.0154	0.0152	0.0154
$\frac{\text{Acid produced per minute}}{\text{Per cent. combined enzyme}}$	0.0116	0.0116	0.0118	0.0117	0.0107	0.0115

The agreement is thus seen to be very good except in the series $a = 5.66$. It was in this series that the calculation of the time taken to produce 1 cc. met with a little difficulty and here the discrepancy may be only an apparent one.

I wish to emphasize that the above calculation is to be regarded as purely hypothetical and only adopted for the purpose of giving a mechanism by which the reaction may be conformed to the mass law. The argument, of course, loses its validity if we do not assume the presence of an intermediate compound, but merely because the results obtained by a highly hypothetical calculation correspond fairly closely with the observations, we must not therefore conclude that an intermediate compound is necessarily present.

It is tacitly assumed in the above argument that the amount of enzyme action is proportional to the amount of enzyme present. This has been shown repeatedly, but it is so essential to my argument that I feel it necessary to give my own observations. We have seen that it is advisable to measure the enzymic activity by the reciprocal of the time taken to produce a given amount of acid, and formulated this as $E = k/t$ or $Et = k$, where $E =$ the enzymic mass in a given volume or the enzymic concentration.

The following table summarizes my results with three different strengths of enzyme and various ester concentrations.

TABLE VII.

Time in minutes to produce x cc. in acid.

	Enzyme = 0.476%.	Enzyme = 0.196%			Enzyme = 0.099%.			
x	$a = 42.77$.	$a = 11.40$	$a = 21.55$.	$a = 31.86$ †	$a = 10.62$	$a = 21.40$.	$a = 32.56$.	$a = 43.53$.
2	.....	10.01	. .	8.92†	20.07	19.27	19.54	19.68
4	.....	22.41	. .	19.9†	45.17	43.26	45.43	45.80
6	.....	37.47*	.....	32.7†	75.78*	70.29	74.27	75.25
8	.....	57.11*	. .	46.8†	121.98*	101.45	106.48	109.69
10	27.14	114.*	66.63	62.2†	249.5*	137.37	143.03	147.41
16	53.27	......	141.8	......	......	......	......	......
20	75.40	......	295.*	......	......	......	......	......

† Temperature was inconstant and experiment was not done in duplicate.

* Concentration of ester is below $N/200$.

TABLE VII (*Continued*).

Time in minutes to produce x cc. of acid × per cent. of enzyme.

	Enzyme = 0.476%.	Enzyme = 0.196%.			Enzyme = 0 099%.			
x.	a = 42 77.	a = 11 40	a = 21 55	a = 31 86.	a = 10.62.	a = 21 40.	a = 32 56.	a = 43 53.
2......	....	1.96	......	1.75†	1.99	1.91	1.93	1.95
4......	....	4.39	......	3.90†	4.48	4.28	4.50	4.53
6......	....	7 34*	......	6.41†	7.50*	6.96	7.35	7.45
8......	....	11.2*	.....	9.17†	12.1*	10.0	10.5	10 9
10......	12.9	22.3*	13.1	12.2†	24.7*	13.6	14.2	14.6
16......	25.4	.....	27.8	....	.....	.....	.....	.....
20......	35 9	....	57.8*	....	.....	.....	.....	.....

† Temperature was inconstant and experiment was not done in duplicate.

* Concentration of ester is below $N/200$.

Leaving out of consideration the figures marked with an asterisk (*) and considering the figures marked with a dagger (†) as only approximate, we see that Et is very nearly a constant for any given concentration of acid, although the enzyme is slightly more active in the 0.476 per cent. series. Practically every investigator who has done carefully planned work with lipase in one or two phase solutions has also concluded that the enzyme activity is proportional to the enzymic concentration.

The main thesis of this paper is that the amount of zymolyte hydrolyzed per instant is independent of the concentration of the zymolyte over a considerable range. This has been shown to be true for invertase by A. Brown,[1] Hudson[2] and Taylor,[3] for diastase by Taylor[3] and for lipase by Kastle and Loevenhart[4] and by Kastle, Johnston and Elvove.[5] Brown also gave a partial explanation of the phenomenon somewhat similar to the one I have given. The peculiarities in the hydrolyses of the ester and cane sugar are due to the enzyme and not to the substances hydrolyzed, since when acids are used as catalytic agents the progress of the action conforms absolutely to the mass law. This has been shown by numerous investigators beginning with Wilhelmy[6] in the case of cane sugar in 1857. Ostwald,[7] among others, has investigated the kinetics of both actions very completely and Cohen[8] has shown that the cause of the apparent deviation of the acid inversion of cane sugar from the monomolecular law is due to the volume of the solution occupied by the sugar. Morse and his co-workers have shown that the osmotic pressure of cane sugar is equal to the gas pressure of a gas occupying the volume of water present in the sugar solution under consideration. Therefore, if in the expression $k = 1/t \log [a/(a - x)]$, we make a and x proportional to the osmotic pressure, instead of to the concentration of the sugar, we will have a very close agreement of k in the different concentrations. The osmotic pressure of the zymolyte cannot be invoked to explain the anomalies which I have noted in the above cases of enzyme action, as the variations of k are in the wrong direction. On the other hand the explanation which I have given or some modification of it, can be invoked to explain the anomalies of the action of invertase and diastase.

---

[1] Brown, *J. Chem. Soc.*, 81, 373 (1902).

[2] Hudson, THIS JOURNAL, 30, 1564 (1908).

[3] Taylor, *J. Biol. Chem.*, 5, 405 (1909).

[4] Kastle and Loevenhart, *Am. Chem. J.*, 24, 491 (1900).

[5] Kastle, Johnston and Elvove, *Ibid.*, 31, 521 (1904).

[6] Wilhelmy, *Pogg. Ann.*, 81, 413 and 499 (1850).

[7] Ostwald, numerous articles in *J. prakt. Chem.* about the year 1885.

[8] Cohen, *Z. physik. Chem.*, 23, 442 (1897).

It may be of interest in this connection to give the results of other investigators bearing on the above statements.

(1) A. Brown.[1]

INVERTASE ACTING ON CANE SUGAR.

	Grams sugar per 100 cc	Grams sugar inverted in 60 min	$1/t \log [a/(a - x)]$.
A	40 02	1.076	
	29 96	1.235	
	19 91	1.335	
	9 85	1.335	
	4 89	1.230	
B.	(2 0)	(0.308)	(0.00132)
	1 0	0.249	0.00219
	0.5	0 129	0 00239
	0.25	0.060	0.00228

Apparently two different enzyme solutions were used. The monomolecular law is followed only in dilute solutions. In the stronger solutions the absolute amount inverted in 60 min. is nearly independent of the sugar concentration. In the three most dilute solutions k is nearly the same but is much smaller in the 2 per cent. solution than in the 1 per cent. solution. Though not calculated for the stronger solutions, it would, of course, be about inversely proportional to the concentration of the sugar.

(2) Hudson.[2]

INVERTASE ACTING ON CANE SUGAR.

Cane sugar per 100 cc.	Grams inverted in 30 minutes per 100 cc. solution.	Grams inverted in 60 minutes per 100 cc solution.
4.55	3.33	4.23[3]
9.09	4.12	6.74
27.3	3.06	6.00

(3) Kastle and Loevenhart.[4]

---

[1] Brown, *J. Chem. Soc.*, 81, 373 (1902), tables on 379 and 387.

[2] Hudson, THIS JOURNAL, 30, 1575 (table).

[3] The concentration of cane sugar was only 1.22 per cent. at the beginning of the second 30 minutes of the reaction.

[4] Kastle and Loevenhart, *Am. Chem. J.*, 24, 514; cf. Kastle, Johnston and Elvove, *Loc. cit.*, 31, 546.

LIPASE ACTING ON ETHYL ACETATE.

Grams ethyl acetate per 5 cc.	Grams ethyl acetate hydrolyzed in 15 minutes per 5 cc. solution.
0.05656	0.003952
0.04242	0.003861
0.02828	0 003952
0.01414	0.003403

The agreement in the three stronger solutions is remarkable.

(4) Taylor[1] gives interesting figures for invertase and diastase. He gives only the reaction constants. These multiplied by the per cent. of the zymolyte show close agreement in the stronger solutions.

INVERTASE ON CANE SUGAR.

Per cent. sugar.	$k \times 10^4$.	$(k \times 10^4) \times$ per cent. sugar.
½	423	212
1	326	326
2	167	334

DIASTASE ON MALTOSE.

Per cent. maltose	$k \times 10^6$.	$(k \times 10^6) \times$ per cent. maltose.
1	363	363
2	239	478
3	142	426

The enzyme action in these three cases is thus seen to differ markedly from the hydrolysis by acids.

Conclusions.

(1) In a solution of given volume and acidity the time taken to hydrolyze a given amount of ethyl butyrate is inversely proportional to the concentration of the enzyme. Under similar conditions of acidity each particle of enzyme hydrolyzes the same absolute amount of ester per instant no matter what the concentration of enzyme.

(2) With a given concentration of enzyme the time taken to hydrolyze a given amount of ethyl butyrate is dependent on the acid concentration but independent of the ester concentration, provided this is above $N/200$. In other words for each concentration of acid a given amount of enzyme hydrolyzes very nearly the same amount of ethyl butyrate over a wide range of ester concentration.

(3) This phenomenon can be conformed to the mass law by assuming that the enzyme and the ester form an intermediate compound, which in concentrations of the ester above $N/200$ contains most of the enzyme.

(4) Assuming that the amount of this intermediate compound at any instant is proportional to the product of the concentration of the free enzyme and the ester, we saw that the rate of acid production was proportional to this quantity. This hypothesis, therefore, is seen to be in perfect accordance with the mass law.

(5) No explanation is offered as to the inhibiting effect of the acid.

(6) The question is raised as to whether the constancy of the function $1/t \log [a/(a-x)]$ in certain cases is not purely accidental.

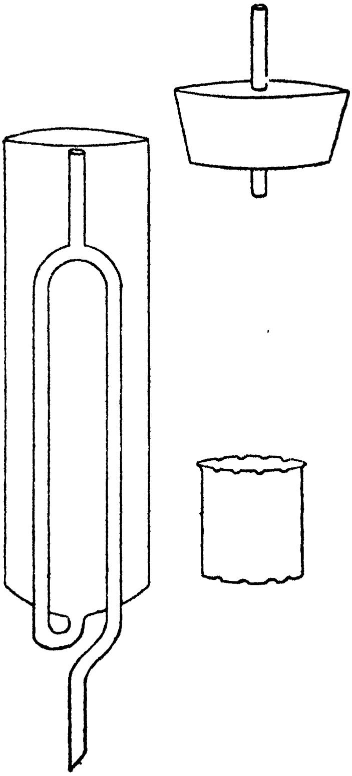
PARISER STRASSE, 38 III, BERLIN.

---

[1] Taylor, *J. Biol. Chem.*, 5, 405 (1910).

NOTE.

Extraction Apparatus.—For the extraction of a substance by means of a mixture of solvents (*e. g.*, 50 per cent. alcohol), distillation and the use of a reflux condenser being inadmissible, I have devised a form of apparatus shown in the accompanying diagram. It consists of a glass tube 4 × 12 cm. terminating at the bottom in an outside siphon tube $9^{1}/_{2}$ cm. long, the upper bend of which has a short open "riser" fitted with a short piece of rubber tubing. A support for the extraction cartridge may be made by cutting off a section about 3 cm. long from the open end of a wide test-tube and indenting its edges.



This support having been inserted, the extraction cartridge with contents is introduced and then the mixed solvent. After standing a sufficient time, the solvent is drained off by clamping the rubber tube attached to the "riser," closing the large tube with a stopper bearing an open glass tube, and forcing air through the latter. The large tube having been drained, the solvent in the extraction cartridge is allowed to drain into the space below it and the siphon again started. In this way, *all* of the solvent can be removed before the second portion is introduced.

Advantages.—(1) There is no stopcock (as in separatory funnels) which may leak or require contaminating grease under the penalty of possible sticking. (2) The siphon action, being under control, makes possible the complete draining of the apparatus between successive extractions and also prevents the undesirable premature draining of the apparatus such as sometimes occurs when the siphon tube becomes filled with a broken column of liquid or when too much solvent is unintentionally introduced and the siphon action thereby started. (3) The apparatus can be stoppered easily and evaporation, with subsequent variation in the proportion of the solvents, prevented.

R. P. Noble.

Indianapolis, Ind.

NEW BOOKS.

Leitfaden für den Unterricht in der anorganischen Chemie didaktisch bearbeitet. VON DR. JOACHIM SPERBER. Dritter Teil. Zurich, Verlag von E. Speidel, 1910. 536 pages.

The first part of this general treatise on inorganic chemistry appeared in 1899 and was reviewed by Prof. Henry Fay in THIS JOURNAL, **22,** 222. The second part appeared in 1901 and was reviewed by Prof. Fay in THIS JOURNAL, **24,** 197. The present volume bears the date 1910 and constitutes the third and final volume of the work.

The first two volumes dealt primarily with the non-metals and general theories of chemistry. The third volume is essentially a discussion of the metals and their compounds. About forty pages at the beginning of the volume are devoted to the halogen and sulphur compounds of the non-metals and a few pages at the end to the periodic law and the author's theory of valence. The periodic classification is adhered to in the order of the discussion of the metals. The treatment is clear and comprehensive and the volume is deserving the same general approval as was given to the earlier volumes by Prof. Fay. In the "Schlussbemerkung" the author states that because of the increased cost in publication some of the illustrations as well as table of contents had to be omitted. The omission of an index from such a publication needs no comment.

WILLIAM MCPHERSON.

Physical Chemistry for the Electrical Engineers. By J. LIVINGSTON R. MORGAN. John Wiley & Sons, 1909. Second edition, revised. $1.50.

It is becoming necessary to offer courses in electrochemistry to electrical engineering students but a considerable knowledge of physical chemistry is a necessary preliminary and as these students are generally lacking in this, Professor Morgan's little book is a welcome supplementary text. The first six chapters (184 pages) are devoted to the properties of gases, solutions, chemical mechanics, equilibrium in electrolytes, etc. The author has followed Ostwald's idea and avoided as much as possible the use of hypotheses and has succeeded in presenting these things concisely but still in an interesting way. Some have questioned the advisability of neglecting our ideas of atoms and molecules since the student is already familiar with this point of view from his beginning chemistry and will come across it in his future contact with things chemical. The objection has some weight; on the other hand the presentation is sufficiently different from what the student might have expected to arouse his interest and attention and this is essential, as otherwise little or nothing is thought out or retained. The essential principles of electrochemistry proper are briefly presented. A more frequent mention of the application of these principles to things which are familiar to the electrical engineer would

add much to the book, particularly should some of the problems be from this standpoint.
G. A. HULETT.

Principles of Chemical Geology. By JAMES VINCENT ELSDEN. London and New York: Whittaker & Co., 1910. pp. vi+220. Cloth.

The title of this book is somewhat misleading, for it is not a general treatise on chemical geology. It is really and professedly an attempt to apply the theory of equilibrium to geological problems, and therefore it covers a well-defined but limited field. The specific questions to which modern physico-chemical ideas and principles are applicable are discussed with some detail in an elementary way, with abundant illustrations of their applicability and a wealth of references to literature. Such themes as viscosity, diffusion, surface tension, vapor pressure, eutectics and solid solutions are considered, and their bearing upon the magma and its solidification are clearly treated. The work of men like LeChatelier, Arrhenius, Doelter, Vogt, Ostwald, van't Hoff and Morozewicz is fully discussed, that of van't Hoff upon the Stassfurt salts being given considerable prominence. English and American workers are also extensively cited, showing that the author has gone quite thoroughly over the available literature. There are, here and there, minor errors in purely chemical and mineralogical matters, but they are so few that they do not lessen the value of the book to any serious extent. The volume will certainly be most helpful to many progressive geologists, for magmatic problems are coming more and more into the field of physical chemistry. What happens when molten rock solidifies, or when a bed of rock salt or gypsum is deposited from solution? Questions like these must be handled by modern methods, and the philosophical geologist can no longer be content with the chemistry of thirty years ago.
F. W. CLARKE.

Beiträge zu einer Kolloidchemie des Lebens. VON RAPHAEL ED. LIESEGANG. Dresden: Verlag von Theodor Steinkopff, 1909. 148 pp. Price, 4 mks.

This is a collection of heterogeneous experiments dealing with the formation of precipitation membranes of various phosphates, silver chloride, copper ferrocyanide, etc., in gelatin, which are supposed to, and possibly do in some particulars, parallel the processes of formation of membranes, growth, partial permeability, and resorption, occurring in living cells.

The experiments are not planned apparently with any definite end in view nor is any explanation given of some of the results. An idea of the scope of the experiments, of which there are one to several included under each heading, may be obtained from a partial list of the chapter headings of Part 1, pp. 1–77. "Apparent membrane effects; the passage of circles of diffusion through each other; speed of diffusion; the apparent attraction of diffusion circles; rhythmic after-diffusion; carbon dioxide development in gelatin; apposition and intersusception; the acid theory of osteomalacia; the growth of hollow bones; rachitis; calcium phosphate membranes; pressure effects; bone archetectonics; hydrogen peroxide and gelatin; researches on nucleic acid." The second part of 78 pages contains more protocols with suggestions of their possible bearing on bone formation, muscle contraction, conduction, etc.

It is sufficient to give a list of the chapter headings and the number of pages to show the necessarily superficial, incomplete and incoördinate character of the work. Almost any one of the titles mentioned would require for any adequate treatment a book of at least the size of this one. The book can not be recommended as an example of what a scientific work should be, but rather, in the reviewer's opinion, as an excellent example of what it should not be. There are no fundamental guiding principles for the experiments, there is no thorough working out of any one thing to see whether the experiments reported really parallel vital phenomena except in a grossly superficial way. Even the title of the book, "Contributions to a Colloidal Chemistry of Life," strikes the reviewer as badly chosen to say the least, since in the first place, life is not to be explained by chemistry even taken as a whole, let alone that part of it dealing with the colloids, and in the second place it is still uncertain that colloids differ in any fundamental particular from noncolloids, so that a separate division of chemistry for them would appear certainly premature. It is possible that the author's industry in trying experiments of precipitation in gelatin, may enable some one to find among the experiments some stones which may be used in erecting a planned building, or he may find here some hints in shaping further work which may be useful but apart from this, the work has little value owing to its incoördinate and inconclusive character.

Any one who feels tempted to publish work of this kind should read any one of Darwin's books, or any book or paper of Claude Bernard, Lavoisier, Faraday, DuBois Raymond, van't Hoff, or any of the great men of science to get a standard of excellence. He will not find that these men publish hodge-podges of this kind, which, alas, are altogether too common in all branches of biological investigation.

ALBERT P. MATHEWS.

RECENT PUBLICATIONS.

ANDOUARD, A.: **Nouveaux eléments de pharmacie.** 8°, 1168 pp., 26 Fr.

ARTHUS, M.: **Elemente der Physiologischen Chemie.** 3 Aufl. Leipzig: 8°, 353 pp., 6, 75 M.

BAYLISS, W. M.: **Das Wesen der Enzymwirkung.** Dresden: T. Steinkopff. 3 M.

Benolt, F.: **La néo-métallurgie, ses moyens et ses methodes.** 92 pp. 3 Fr.

Berthier, A.: **L'éclairage industriel.** 4°, 140 pp., 7.50 Fr.

Bertrand, G., and Thomas, P.: **Guide pour les manipulations de chimie biologique.** Paris: 12°, 372 pp., 6 M

Blouet, M : **Nouvelles manipulations de chimie.** 16°, 202 pp., 2.50 Fr

Bollenbach, H.: **Neue massanalytische Methoden zur Bestimmung von Eisen und Blei.** Böhm, 1.50 m.

Bollenbach, H : **Laboratoriumsbuch für die Tonindustrie.** Halle, 8°, 90 pp., 3.60 M.

Bronn, J.: **Der elektrische Ofen.** Halle a S. 22 M

Burghardt, R · **Praktische Anleitung zur Inbetriebsetzung Hoffmannscher Ringofen.** Halle, a S. 2.40 M.

Buzenac. **Etude sur la corrosion des métaux.** 3.50 Fr.

Calmette, A.. **Recherches sur l'épuration biologique et chimique des eaux d'égout.** 5 Bd. 8°, 172 pp., 6 Fr.

Chowlson, O. D.: **Traité de physique.** Bd. 4 430 pp., 12 Fr.

Coles-Finch, W **Water, its Origin and Use.** New York: Van Nostrand, 8°, 504 pp., $5.00.

Crookes, Sir William · **On Scandium.** Part 2. Dulau 4°, 1s, 6d.

Dammer, O.: **Chemische Technologie der Neuzeit.** In 12–13 Liefer., je 6 M. Stuttgart · Ferd. Enke

Delbruck, M **Illustriertes Brauerei-Lexikon.** Berlin: Paul Parey, 30 M.

Dennstedt, M **Anleitung zur vereinfachten Elementaranalyse fur wissenschaftliche und technische Zwecke.** 3 Aufl Hamburg O Meissner, 3 M.

Dietrich, H **Untersuchungen über die bei der Elektrolyse von Nickelsalzen auftretenden periodischen Erscheinungen.** Munster 8°, 94 pp., 3 M

Duhamel, G · **L'acide thyminique** (Solurol). 8°, 156 pp., 3 Fr.

Elsden, J V : **Principles of Chemical Geology.** Whittaker, 8°, 230 pp., 5 s.

Erben, F.. **Vergiftungen, Klinischer Teil.** 2 Halfte **Die organischen Gifte.** Wien W. Braumuller, 1245 pp , 38 M.

Fauvelle : **La physico-chimie.** Paris 2.45 Fr

Frémont, C.: **Essais des fers et des aciers par corrosion.** 4°, 56 pp., 2 Fr.

Friend, J. N.· **An Introduction to the Chemistry of Paints, with Diagrams.** Longmans, 8°, 214 pp., 3 s, 6 d.

Garton, F. R · **A High School Course in Physics.** Appleton, 8°, 5 s.

Gissing, C. E. **Spark Spectra of the Metals.** London: Baillière, Tindall, and Cox. 4°, 7 s, 6 d.

Grimmer, W.· **Chemie und Physiologie der Milch.** Berlin · Paul Parey 10 M.

Guilleminot, H : **Rayons X et radiations diverses.** 318 pp., 5 Fr

Heiduschka, A., and Pfizenmaier, K.: **Beitrage zur Chemie u. Analyse der Fette.** München 8°, 50 pp.

Hünlich: **Anleitung zur Unterscheidung von Textilmaterialen.** Roda: 8°, 45 pp., 1 M.

Iron-ore Resources of the World. New York: Lemcke and Buechner, 8°, $20.00.

Jaksch, R. v.: **Die Vergiftungen.** 2 Aufl. Wien: 8°, 732 pp., 16 M.

KAHANE, M.: **Die Arzneitherapie der Gegenwart.** Wien: Urban and Schwarzenberg, 8°, 10.50 M.

KASSEL, R.: **Viskosität binarer Flussigkeitsgemische.** Wien: J. Eisenstein & Co. 50 pp., 1.80 M.

KOHL, F. G.: **Ueber das Wesen der Alkoholgärung.** Dresden: 8°, 14 pp., 1 M.

KRAUS, A., AND SCHWENZER, P.: **Hilfstabelle für Nahrungsmittelchemiker.** Berlin: 12°, 100 pp., 2 M.

KURZ, K.: **Der Radiumvorrat der Natur.** München: 8°, 31 pp., 1M.

LACHAUD, M: **Nouvelle théorie des sciences physiques. Unité de la matière, étude des fluides, force, travail, energies rayonnantes, électricité.** 8°, 152 pp., 3.50 Fr.

LANGE, H.: **Studien über die Zusammensetzung heliumführender Mineralien.** Halle a. S. 34 pp.

LEHMANN, F.: **Ueber massanalytische Methoden zur Bestimmung der Zuckerarten.** Marburg: 8°, 56 pp., 1.50 M.

LEISER, R.: **Elektrische Doppelbrechung der Kohlenstoffverbindungen.** Halle a. S. 3.60 M.

LENHARTZ, H.: **Mikroskopie und Chemie am Krankenbett.** 6, Aufl. Berlin: 8°, 429 pp., 9 M.

LINDNER, P.: **Atlas der mikroskopischen Grundlagen der Gärungskunde.** 2 Aufl. Berlin: Paul Parey, 8°, 19 M.

LODIN: **Note sur la fabrication électrolytique de l'aluminium.** 8°, 68 pp., 2.50 Fr.

LORD, J. P.: **Radium.** London: 8°, 103 pp., 2.70 M.

LÖWENSTEIN, E.: **Ueber Hydrate, deren Dampfspannung sich kontinuierlich mit der Zusammensetzung ändert.** Hamburg: 8°, 73 pp.

MACH, E.: **Populärwissenschaftliche Vorlesungen.** 4. Aufl. Leipzig: 8°, 508 pp., 6.80 M.

MASING, G.: **Ueber die Bildung von Legierungen durch Druck und über die Reactionsfähigkeit der Metalle im festen Zustande.** Hamburg: 8°, 47 pp.

MAURALN, C.: **Les états physiques de la matière.** 16°, 328 pp., 3.50 Fr.

MCMILLAN, W. G.: **A Treatise on Electrometallurgy.** 3rd Ed. Griffin, 8°, 442 pp., 12 s, 6 d.

MEDICUS, L.: **Einleitung in die Chemische Analyse.** (4 Hefte) Tübingen: 8°, 193 pp., 2 M.

MENDELÉEF, D.: **Versuch einer chemischen Aufflassung des Weltäthers.** 2 Aufl. St. Petersburg: 8°, 54 pp., 1.50 M.

MEUSEL, E.: **Die Materie der chemischen Elemente und das Wesen der chemischen Reaction.** Liegnitz: 8°, 64 pp., 2.50 M.

MEYER, F.: **Die Technik der Verbrennung und Energiegewinnung aus städtischen Abfallstoffen.** Leipzig: F. Leineweber, 24 pp., 2.50 M.

MINZ, S. G.: **Zur Frage von dem Einfluss der Milchnahrung auf den stickstoff- und Phosphorumsatz.** Petersburg: 116 pp.

MITCHELL, C. A.: **Oil.** London and New York: Sir Isaac Pitman and Sons.

MOLISCH, H.: **Die Eisenbakterien.** Jena: G. Fischer, 83 pp., 5 M.

NIERENSTEIN, M.: **Chemie der Gerbstoffe.** Stuttgart: Ferd. Enke, 58 pp., 120 M.

Oscroft, P. W., and Shea, R. P.: **A Manual of Elementary Practical Chemistry.** Rivingtons, 8°, 142 pp., 2 s.

Ostwald, W.: **Die Forderung des Tages.** Leipzig: 8°, 609 pp., 9.30 M.

Ottersbach, G.: **Buchheisters Vorschriftenbuch für Drogisten.** 6 Aufl. Berlin: Julius Springer, 724 pp., 10.40 M.

Parma, A.: **Ueber ökonomischen Kohlenverbrauch.** Teplitz-Schonau: A. Becker, 8°, 56 pp., 2 M.

Pécheux, H.: **Précis de metallurgie.** 490 pp., 5 Fr.

Percival: **Agricultural Bacteriology, Theoretical and Practical.** Duckworth, 8°, 48 pp., 7 s, 6 d.

Peyre, R.: **La céramique française.** 8°, 310 pp., 3.50 Fr.

Philip, J. C.: **Physical Chemistry; its Bearing on Biology and Medicine.** London E. Arnold, 8°, 7 s, 6 d.

Piest, C.: **Die Cellulose.** Ihre Verarbeitung und ihre chemischen Eigenschaften. Stuttgart: 8°, 157 pp., 6 M.

Proumen, H. J.: **La matière, l'éther, l'électricité.** 2 Bd., 12°, 302 pp., 7 Fr.

Rechenberg, C. v.: **Theorie der Gewinnung und Trennung der ätherischen Oele durch Destillation.** Miltitz. 8°, 493 pp., 12.50 M.

Reid, J.: **Practical Sanitation.** 15th Ed. London: C. Griffen & Co.

Renker, M.: **Ueber Bestimmungsmethoden der Cellulose.** 4 Aufl. Berlin: 8°, 107 pp., 2.80 M.

Rettberg, H.: **I. Abbau des Morphobetains. II. Ueber einige Additionsprodukte cyclischer Basen mit Hydrochinon.** Berlin: R. Trenkel. 8°, 35 pp., 2 M.

Richter, M. M.: **Lexikon der Kohlenstoffverbindungen.** 3 Aufl. (30 Lieferungen.) Hamburg: 8°, Jede Lieferung, 6 M.

Richter, V. v.: **Lehrbuch der Anorganischen Chemie.** 12 Aufl. Bonn: 8°, 10 M.

Riesenfeld, E. H.: **Anorganisch-chemisches Praktikum. Qualitative Analyse und anorganische Präparate.** Leipzig: 8°, 6 M.

Rievel, H.: **Handbuch der Milchkunde.** Hanover. H. Schafer, 2 Aufl. 12.50 M.

Rivals, P., and Devaud, M.: **Chemie.** 2 T., 216 pp., 2 Fr.

Rosanow, N.: **Kursus der physiologischen Chemie mit Anleitung zur qualitativen und quantitativen Analyse des Harns.** 2 Aufl. Kasan: 8°, 155 pp., 1.35 Rbl.

Scheffler, W.: **Einrichtung von Fabriklaboratorien.** Hannover: 8°, 146 pp., 3.40 M.

Scholtz, M.: **Lehrbuch der Pharmazeutischen Chemie. Teil I: Anorganischer Teil.** Heidelberg: 8°, 11.50 M.

Seligmann, F., and Tieke, E.: **Handbuch der Lach- und Firnis-Industrie.** Berlin: Union, Deutsche Verlagsgesellschaft. 30 M.

Smiles, S.: **The Relations between Chemical Constitution and Some Physical Properties.** London: John Long, 8°, 6 s.

Sommer, E.: **Ueber die Radioaktivitätsverhältnisse der natürlichen Heilquellen des Deutschen Sprachgebietes.** München: 4°, 58 pp., 2 M.

Steensma, F. A.: **Methoden der chemische en microscopische Diagnostiek.** Amsterdam: Scheltema & Holkema, 8°, 2.50 fl.

SCHENK, E.: **Ueber die Reduktion von Pinen zu Pinan; Eigenschaften und chem. Verhalten des letzteren.** Hildesheim: August Lax, 2 M.

STRZYZOWSKI, C.: **Cours de chemie physiologique et pathologique.** 8°, 160 pp., 5 Fr.

THOMS, H.: **Arbeiten aus dem pharmazeutischen Institut der Universität Berlin.** Wien: Urban and Schwarzenberg, 7 Bd., 312 pp., 8.50 M.

THOMAS, V.· **Guide pratique de teinture moderne, suivi de l'art du teinturier-dégraisseur.** Paris: 8°, 16 M.

TILLIER, L.: **Le caoutchouc.** 8°, 34 pp., 1.25 Fr.

TOWNSEND, J. S.: **The Theory and Ionization of Gases by Collosion.** Constable, 8°, 100 pp., 3 s, 6 d.

TRÖGELE, F.: **Über das Verhalten der Alkaloide in den Organen der Atropa belladonna L.** Mikrochemische und quantitative Untersuchung. Berlin: R. Trenkel, 88 pp., 2 M.

WALLACE, R. C.: **Ueber die binären Systeme des Natriummetasilicats mit Lithium-, Magnesium-, Calcium-, Strontium-, und Bariummetasilicat.** Hamburg: 8°, 52 pp., 2.50 M.

WEIL, S. F.: **Ueber Asphalt- und verwandte Industrien.** Wien: J. Eisenstein, 64 pp., 1.25 M.

WHITNEY, M.: **Fertilizers for Wheat Soils.** Washington: Government Printing Office.

WINTERSTEIN, E., AND TRIER, G.: **Die Alkaloide; eine Monographie der natürlichen Basen.** Berlin: Borntrâger. 8°, 340 pp., 12.20 M.

WOLFF, J.: **Contribution a la connaissance de divers phénomènes oxydasiques naturels et artificiels.** Paris: 8°, 99 pp.

WYSSOZKY, W. F.: **Ueber die Bindung der Derivate des Jods an das Gewebe der Leber.** Petersburg: 8°, 128 pp.

VOL. XXXII. DECEMBER, 1910. NO. 12.

THE JOURNAL

OF THE

American Chemical Society

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

STUDIES IN VAPOR PRESSURE, VI: A QUANTITATIVE STUDY OF THE CONSTITUTION OF CALOMEL VAPOR.

BY ALEXANDER SMITH AND ALAN W. C. MENZIES.

Received October 15, 1910.

Numerous determinations of the vapor density of calomel at atmospheric pressure have shown, within the limits of error of the methods, that the density corresponds to the formula HgCl. Odling[1] was the first to show, by the amalgamation of a gold-leaf dipped in the vapor, that free mercury was present. The vapor was, therefore, at least partly composed of a mixture of $Hg + HgCl_2$, in equimolecular proportions, which would have the same density as HgCl. Debray[2] could find no amalgamation at 400°, but Brereton Baker[3] obtained it at 445°. Erlenmeyer[4] condensed the vapor rapidly on a tube filled with cold mercury, but found less than 0 03 g. of free mercury in the large deposit of sublimed calomel. Debray secured a similar result with a gilded, silver U-tube containing running water. The presence of free mercury was therefore established, but the evidence, so far as it went, demonstrated only a small amount of dissociation.

Harris and V. Meyer,[5] after confirming by a number of determinations the value of the vapor density previously accepted, attempted in two ways to ascertain the amount of dissociation. In the first place, by heating calomel at about 465° in a porous vessel enclosed in a wider glass tube, they secured, by diffusion, a "dense mass" of free mercury in the cold part of the outer tube and a "considerable amount" of corrosive sublimate in the residue remaining in the porcelain cell. They infer that this proves "copious dissociation" in calomel vapor. It is obvious, however, that a very small degree of dissociation in the vapor would account for this result equally well. The exit of the mercury through the pores would be expected to disturb a state of equilibrium between the undissociated calomel and the dissociation products, and to result in the final liberation of a far larger proportion of mercury than that contained in the original vapor. This experiment, and another of a similar nature, therefore, in reality only confirmed Odling's proof that some free mercury was present, without in the least degree indicating its amount. The question whether the proportion of undecomposed HgCl in the vapor was over 90 per cent. or zero remained unanswered.

---

[1] *J. Chem. Soc.*, **3**, 211.

[2] *Compt. rend.*, **83**, 330.

[3] *J. Chem. Soc.*, **77**, 646.

[4] *Ann.*, **131**, 124.

[5] *Ber.*, **27**, 1842 (1894).

The experiment just described being of a physical nature, Harris and Meyer sought confirmation by chemical means of the (unwarranted) conclusion they had drawn from it. They assume that a vapor largely composed of HgCl should give the reactions of a mercurous salt, while one composed largely of Hg and $HgCl_2$ should give the reactions of a mercuric salt. A rod coated with solid caustic potash, and preheated in an empty test tube (240–260°), was quickly immersed in the vapor of calomel contained in another tube at the same temperature. A yellowish red layer of mercuric oxide appeared immediately. The authors recognize the fact that mercurous oxide is unstable at this temperature, but seem to think it would necessarily have been formed *as a transient stage* if HgCl had been present. They smeared a similar rod with mercurous oxide and, preheating being out of the question, dipped it, cold, into the calomel vapor. After a "long (*geraumer*) time—15–25 seconds," the color changed to yellow owing to the decomposition of the oxide into Hg + HgO. The conclusion drawn from these two experiments is that, since not even a trace of transient darkening was observed with the potash, the mercuric oxide could not have arisen from previously formed mercurous oxide, but must have been the direct product of interaction with the calomel vapor. This mild inference is doubtless correct. But the following clause, stating that the vapor therefore contains the combined mercury as mercuric chloride, indicates complete confusion of thought. Since mercurous oxide is unstable at 240–260°, why should its formation be counted upon under any circumstances at this temperature? True, metastable substances are sometimes produced, but more often they are not. In this case, certainly, the deposition of mercuric oxide would be quite as natural with a vapor wholly composed of a mercurous compound as with one wholly composed of a mercuric salt.

On an experimental foundation which, to say the least, is thus eminently inconclusive, the authors base their final statement: "In vaporizing, calomel decomposes completely according to the equation $Hg_2Cl_2 = Hg + HgCl_2$." This conclusion, that no HgCl is contained in the vapor, by reason of the confidence with which it is stated, has been very generally accepted, and is the view universally held by chemists. Since it was published, no further investigation of the matter seems to have been made. The controversy with Fileti[1] which arose out of this paper, added nothing regarding the possibility of the presence of calomel, as such, in the vapor. It did draw from V. Meyer the statement that he had "never made the mistake of holding that *his experiments* with calomel furnished proof of the double formula," but we are not here concerned with the left-hand side of the equation quoted above. It afforded, also, additional proofs that V. Meyer did not fully understand the principles of chemical equilibrium involved in the problem he had undertaken to solve.

The important fact discovered since V. Meyer's work is that noted by Brereton Baker (*l. c.*), namely, that, in the vapor of *carefully dried* calomel, a gold leaf is not amalgamated. If this observation could be accepted as proving the entire absence of free mercury from the vapor, it would demonstrate conclusively the presence of HgCl, at least in the vapor of the dried substance. This inference follows from the fact that the density of Hg_2Cl_2 is 16 26 (air = 1), while the mean of Baker's measurements with dried calomel is only 15. Thus, if there was no dissociation into $Hg + HgCl_2$, two molecules in every 13 (or 15 4 per cent. of the total molecules) were HgCl. We have seen, however, that the gold-leaf test is uncertain, and it would therefore be unsafe to draw any such conclusion.

An examination of the literature thus reveals the fact that, at the present time, no experimental data exist on which can be based an inference, or even a guess, in regard to the proportion of dissociated ($Hg + HgCl$) to undissociated (HgCl) molecules in calomel vapor.

Theory of the Method Used to Solve the Problem.—The inconclusiveness of the previous investigations is due chiefly to two facts, namely, that the problem is a quantitative one, while the experiments directed to its solution were all qualitative, and that the experiments and the reasoning applied to the observations were ill considered. If we assume for the present that a polymolecular form of calomel (say Hg_2Cl_2) is present in the vapor only in negligible amounts, or is absent entirely, as the vapor density determinations seem to show, then there are at most three substances present in the vapor, namely HgCl, Hg, and $HgCl_2$. Their relations in the *saturated* vapor, when solid calomel is in equilibrium with the gases, is shown by the following scheme of equilibria:

---

[1] Fileti, *Gazz. chim. ital.*, 11, 341 (1881), *J. prakt. Chem.*, [2] 50, 222; 51, 197. V Meyer, *Ber.*, 27, 3143; 28, 364

$$\text{Calomel (solid)} \rightleftarrows 2\text{HgCl (vapor)} \rightleftarrows \text{Hg} + \text{HgCl}_2.$$

There are three unknown quantities, namely the partial pressures of HgCl, of Hg, and of $HgCl_2$. Three independent observations are required, theoretically, for the measurement of the values of these three quantities at a given temperature. The three observations which appeared to be most suitable were:

1. The vapor pressure of calomel, P_{calom}. This gives the total value of the three partial pressures.

2. The joint vapor pressure of a mixture of calomel and mercury, with both substances in excess, $P_{\text{mixt.}}$.

3. The vapor pressure of mercury alone, $P_{\text{merc.}}$.

The results of these three measurements are related in such a way that, with the help of the fundamental laws of chemical equilibrium, the three partial pressures may be calculated from them. It is more convenient, however, to handle the resulting data in another way, namely, by considering first the two extreme cases.

If we first assume the proportion of free mercury in calomel vapor to be exceedingly small, and the dissociation therefore to be negligible, then the vapor of calomel is essentially composed of HgCl, and the relation between the observed data is simple. Each single substance (Exps. 1 and 3), at a fixed temperature, gives a fixed vapor pressure. The concentration of the vapor, which determins the vapor pressure, cannot be permanently altered so long as the solid, or liquid, phase is present. In the mixture (Exp. 2), if the liquid mercury and the solid calomel are immiscible, as they appear to be (see, however, below), and if there is no chemical interaction between their vapors (and there is none), and if the vapors have no component in common (a condition fulfilled in that absence of dissociation which we are for the moment assuming), then the vapor pressure of the mixture must be sensibly equal to the sum of the vapor pressures of mercury and of calomel as measured separately at the same temperature, that is:

$$P_{\text{mixt.}} = P_{\text{merc}} + P_{\text{calom.}}. \qquad (1)$$

If, on the other hand, we assume that the dissociation is complete, then HgCl is absent from the vapor: Calomel (solid) $\rightleftarrows$ Hg + $HgCl_2$, and the vapor pressure of calomel (Exp. 1) is made up of only two partial pressures:

$$P_{\text{calom.}} = p_{\text{merc.}} + p_{\text{corros.}}.$$

In this instance, with the mixture (Exp. 2) the mercury and the calomel both furnish mercury vapor, but the fact that the latter is also giving off mercury does not cause a permanent increase in the total concentration of mercury vapor beyond that which mercury by itself can give. The partial pressure of mercury vapor in the mixture is fixed by the presence of the free, liquid mercury at a value identical with the vapor pressure of mercury in the absence of calomel at the same temperature. Hence:

$$P_{\text{mixt}} = P_{\text{merc.}} + p'_{\text{corros.}} \qquad (2)$$

Here the partial pressure of corrosive sublimate in the mixed vapors is determind by the chemical equilibrium between the dissociation products of calomel. Now with pure calomel:

$$p_{\text{merc.}} = p_{\text{corros.}} = \tfrac{1}{2} P_{\text{calom.}}$$

and the value of the calomel dissociation constant is:

$$p_{\text{merc}} \times p_{\text{corros.}} = \text{const.} = (\tfrac{1}{2} P_{\text{calom.}})^2.$$

In the mixture, the constant, and therefore the product of the partial pressures, must have the same value, so that:

$$P_{\text{merc.}} \times p'_{\text{corros.}} = (\tfrac{1}{2} P_{\text{calom.}})^2$$

and

$$p'_{\text{corros.}} = (\tfrac{1}{2} P_{\text{calom.}})^2 \div P_{\text{merc.}}.$$

Hence, substituting in equation 2, the vapor pressure of the mixture is:

$$P_{\text{mixt}} = P_{\text{merc}} + \frac{(\tfrac{1}{2} P_{\text{calom.}})^2}{P_{\text{merc.}}}. \qquad (3)$$

Thus the vapor pressure of the mixture can be calculated (equation 1 for no dissociation, equation 3 for complete dissociation) from the vapor pressures of calomel and mercury measured separately, and can also be observed directly. If either of these extreme cases represents the facts, then the agreement of the calculated with the observed data will show which assumption is correct.

It will be noted that the assumption that the dissociation is negligible gives the greatest value for the total pressure for the mixture. The assumption that the dissociation is complete gives the minimum value for the same total pressure. If HgCl is present, a value between these two will be found. In case intermediate values are obtained, then the partial pressure (p_{calom}) of undecomposed calomel, HgCl, can be calculated from the relation:

$$p_{\text{calom.}} = P_{\text{calom}} - 2\left[P_{\text{merc.}} \pm \sqrt{(P_{\text{mixt}} - P_{\text{calom.}})\, P_{\text{merc.}}}\right], \qquad (4)$$

of which equation 3 is the particular case when $p_{\text{calom.}} = 0$.

At the time, about ten years ago, when this mode of solving the problem first presented itself to one of us, no suitable and simple method of measuring vapor pressures was known, and a higher degree of accuracy was required than any of the known methods seemed to possess at the vaporizing point of calomel. Methods involving confinement over mercury were excluded, because the value of the vapor pressure of calomel in the absence of mercury was required. Ramsay and Young's dynamic method was not sufficiently accurate, as their results with a dissociating solid of similar volatility—ammonium chloride[1]—showed. The spiral gage alone seemed applicable, but the difficulties connected with its use were deterrent. It was with the object of finding simple methods, applicable to solids and to difficult cases, and at the same time accurate enough to be employed in quantitative chemical work, and therefore suitable for the solution of the calomel problem, that the whole study of methods of determining vapor pressures was undertaken. These methods have already been described. Of the three vapor pressures, a knowledge of which was required, only that of mercury had been measured. But the data given by different observers were so discordant that a redetermination of even these values[2] was necessary.

The Vapor Pressures of Calomel.—The vapor pressures of calomel[3] were determined with the static isoteniscope, using the mixture of potassium and sodium nitrates as the confining fluid, as well as in the bath. The isoteniscope, platinum resistance thermometer, and the other parts of the apparatus, and the manipulation, and the corrections and precautions employed, were all identical with those described in connection with the work on water[4] and used again in the work on mercury (*l. c.*). The slow interaction with the nitrates of the mercuric chloride in the vapor results in the gradual production of a slight precipitate of mercuric oxide. But the presence of this precipitate in no way interferes with the use of the liquid as a confining fluid. On the other hand, the resulting accumulation of a slight excess of mercury in the vapor, since it occurs at a point remote from the calomel in the bulb, does no harm. Diffusion of this mercury back into the bulb and its penetration to the surface of the calomel would be required in order that it might disturb the equilibrium and affect the vapor pressure. The excess of mercury is formed so slowly, and the diffusion of mercury vapor is in itself so very slow, that prolonged waiting would be required for the development of any effect. Hence, even if the method did not provide, as it does provide, for the complete expulsion of all the accumulated vapor, and its replacement by a fresh supply, immediately before each reading, no slow increase in pressure would arise from this cause. In point of fact, none was ever observed.

The dynamic isoteniscope[5] would have been selected, instead of the static one, but for the fact that to secure strictly comparable results it was desirable to employ static methods for all three determinations.

---

[1] See this series, No 5, THIS JOURNAL, 32, 1454 (1910).

[2] This series, No. 4, THIS JOURNAL, 32, 1434 (1910).

[3] Previous measurements by E. Wiedemann and Stelzner, *Ber. deut. physik. Ges.*, 3, 159 (1905), from 90–180°, by a dynamic method which they used also for iodine; criticized, this series, No. 3, THIS JOURNAL, 32, 1414.

[4] This series, No. 3, THIS JOURNAL, 32, 1419 (1910).

[5] This series, No. 5, THIS JOURNAL, 32, 1448 (1910).

Had the interaction with the nitrates been more rapid, or the vapor more swiftly diffusible, the use of the dynamic form of apparatus would have been necessary for exactness.

The observed vapor pressures are reduced to mm. of mercury at 0° and the sea level at 45° latitude. The temperatures are on the thermodynamic scale, assuming the sulphur boiling point as 445°:

t	*p*	*t.*	*p.*
361.82	454.7	388.11	866.7
371.07	563.7	403.79	1229.7
380.41	724.6		

The values at every 5°, obtained by graphic interpolation, are given in the table towards the end of this paper. The boiling point (760 mm.), taken from the curve, is 382.5°.[1]

The Vapor Pressures of a Mixture of Calomel and Mercury.—The vapor pressure of the mixture was not observed directly, because a small error in temperature would have caused an error of many millimeters in the pressure. Instead, we measured the difference in pressure between the mixture and pure mercury, and small changes in temperature cause very slight alterations in this difference. The observed difference was then added to the vapor pressure of mercury at the same temperature. The chief source of error in the resulting observed pressures of the mixture lies, therefore, in the values of the vapor pressures of mercury. Now, the latter enter also as the chief term in the calculated pressures of the mixture, and in the final comparison of observed and calculated pressures of the mixture this error, therefore, largely disappears.

To accomplish the measurements of the difference, two static isoteniscopes, one containing pure mercury and the other containing the mixture, were immersed together in the bath, and were manipulated simultaneously. One was connected with the gage in the usual way. By means of a bent glass tube fused on to the long, open limb of the gage, the other isoteniscope was connected with the other side of this instrument. The pressures acted against one another, through the gage, and only the differences in pressure was shown.

In this instance, since there was free mercury mixed with the calomel, there was no objection to the use of mercury as the confining fluid. Hence, mercury was used as the confining liquid in both isoteniscopes.

The observed differences in pressure were as follows:

t	*p.*	*t*	*p*
326.7	13.0	386.3	94.4
356.6	36.7	393.9	118.5
374.9	66.8	397.8	135.5

---

[1] Jonker, *Chem. Weekblad.*, 6, 1035 (1909), finds 373°; Harris and Meyer, *Ibid.*, find 357°.

The following table gives the values of these differences at every 5°, obtained graphically, together with the vapor pressures of the mixture, secured by adding these differences to the vapor pressures of pure mercury at the same temperatures:

t.	Diff. ($P_{\text{mixt.}}$ —$P_{\text{merc.}}$).	$P_{\text{mixt.}}$, obsd.	t.	Diff. ($P_{\text{mixt.}}$ —$P_{\text{merc.}}$).	$P_{\text{mixt.}}$, obsd.
360°	41.0	843.6	385°	90.8	1321.7
365	48.2	924.9	390	105.7	1441.4
370	56.8	1013.0	395	123.7	1570.8
375	66.8	1108.4	400	147.3	1713.4
380	78.1	1211.1			

An Unexpected Complication of the Problem.—In order that the purpose of the experiments next to be described may be understood, a preliminary examination of the foregoing results is necessary. At 390° (data in final table), for example, the vapor pressure of mercury alone ($P_{\text{merc.}}$) is 1335.4 mm. and that of calomel ($P_{\text{calom.}}$) is 906 mm. Assuming complete dissociation, and substituting in equation 3,

$$p'_{\text{corros}} = \frac{(\frac{1}{2}P_{\text{calom.}})^2}{P_{\text{merc.}}} = \frac{453^2}{1335.4} = 153.7 \text{ mm.},$$

we obtain 153.7 mm. for the partial pressure of the mercuric chloride vapor in the mixture at 390°, as calculated, with the aid of the theory, from the vapor pressures of the substances observed separately. The directly observed value of the vapor pressure of mercuric chloride at this temperature, which, again assuming complete dissociation, is the difference between the vapor pressures of the mixture and of mercury alone, is only 105.7 mm. (see table above), a discrepancy of over 30 per cent.

The discrepancy is in an unexpected direction. The total pressure of the mixture, calculated on the assumption that there is no dissociation (equation 1) is 1335.4 + 906 = 2241.4 mm., and calculated on the assumption that dissociation is complete is 1335.4 + 153.7 = 1489.1. The observed pressure of the mixture is 1335.4 + 105.7 = 1441.1. If HgCl were present in the vapor, the total pressure would lie at some point between the two calculated values. The observed pressure is *lower* than the smaller of the two, and below the minimum indicated by the theory as thus far considered. HgCl certainly appeared to be proved absent, but before definitly drawing this conclusion it was desirable to account, if possible, for the lack of agreement between the calculated and observed values. A discrepancy of 48 mm. in a total of 1441 mm., or 3.3 per cent., is not unusual in vapor pressure measurements at high temperatures. But the precautions taken and the tests of the method which had been made, rendered it certain that the errors of observation were of nothing like this magnitude. The cause evidently lay in the nature of the substances.

The Density of Saturated Mercury Vapor.—In the first place, it will be noted that the laws of chemical equilibrium employed hold for the actual concentrations of the substances concerned. The *pressures* are substituted in the formulas, on the assumption that they are proportional to the molecular concentrations. Now, that assumption, which is equivalent to assuming that the substances have normal vapor densities, may not be correct in the particular cases under consideration. For example, it was possible that saturated mercury vapor might have an abnormally high vapor density, and that this substance, while being present in the molecular concentration required by the theory of chemical equilibrium, exercised a pressure less than that proper to its concentration. Thus, in the equation from which the partial pressure of mercuric

$$\frac{(\frac{1}{2}P_{\text{calom.}})^2}{P_{\text{merc.}}} = p'_{\text{corros.}},$$

chloride is calculated, the actual concentration of the mercury may be correct, but its pressure (in the denominator) may be too small. This would account for the calculated value of the whole expression being 153.7 mm., while the observed pressure of $HgCl_2$ is only 105.7 mm. That the density of the saturated mercury vapor should be thirty per cent. too high seemed unlikely, but some considerable part of the divergence might originate here.

The only published determinations of the density of saturated mercury vapor seem to be those of Jewett.[1] His work, however, only shows that the density is approximately normal. A divergence of four per cent. would not have been detected with certainty. Then, too, his observations only extended up to 325° where the vapor pressure is about half an atmosphere, and the divergence, if it existed, might be greater at the pressures of nearly two atmospheres occurring in these experiments. Some measurements were, therefore, made at 360 to 400° (pressures 800–1565 mm.). Jewett's method was used, with modifications in the apparatus calculated to insure a degree of accuracy of ±2 per cent., which was sufficient for the present purpose. The divergence was found to be only about 1 per cent. Hence, within the limits of accuracy of the method, the density is normal under these conditions. This hypothesis, therefore, would not account for divergence encountered in the calomel problem.

As the vapor density of saturated mercury vapor is worth studying on its own account, it is proposed to make a more accurate series of measurements in the near future.

The Density of Saturated Calomel Vapor.—Since the vapor pressure of the calomel enters into the numerator of the fraction, any abnormality in the density of the saturated vapor of this substance would involve a correction which would only increase the divergence of which an explanation was being sought. At the same time, the assumption, that concentration and pressure were proportional to one another, was so fundamental to the whole investigation that it seemed necessary to test it in each case.

---

[1] *Phil. Mag.*, [6] 4, 546 (1902).

The vapor density of saturated calomel vapor has never been determind. In the vapor density measurements of Mitscherlich (508°), Deville and Troost (445°), and V. Meyer and Harris (445° and 518°), made at atmospheric pressure, the vapor was much less than half saturated.

For the determination, a small bulb containing a known weight of calomel was fused on to the neck of a round-bottom flask, after the neck of the latter had been drawn out to a capillary and bent downwards (Fig. 1). The flask was exhausted to less than 0.01 mm. pressure through a side tube, which was then sealed off. The whole was immersed in a vigorously stirred bath of the melted nitrates of potassium and sodium, and the temperature was slowly raised to 352.5°, where it was maintained for ten minutes. The bulb was then raised so that, as the highly arched capillary tube emerged from the surface of the melt, it encountered a blowpipe flame which sealed the capillary. The method of sealing the communication between the bulb and the flask is very essential and was adopted after previous experience had shown that cooling the whole apparatus with this tube open (after the manner of Jewett's experiments with sodium) gave rise to slightly variable results. This variability was due, doubtless, to distillation, caused by unequal rates of cooling of the two very dissimilar parts of the apparatus. The weight of the calomel vapor was determind by finding the loss which the amount in the small bulb had sustained. The volume of the flask was measured by weighing full of air and of water, with reduction to vacuum, and was corrected for the expansion of the glass at 352°. The temperature was ascertained with a nitrogen-filled mercury thermometer[1] and was fully corrected. The vapor pressure of calomel, as determind with the same instrument, was therefore employed (352 mm. at 352.5°). The measurement is accurate within less than ±2 per cent., which was sufficient for the purpose. The densities were: observed 0.002169, calculated 0.002125, and their ratio 1.02. The density was therefore normal, within the errors of measurement.

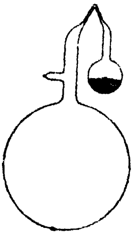


Fig. 1.

Other measurements of the density of saturated calomel vapor have since been made for another purpose, and will be published in another paper. The values confirm the conclusion that the density is normal.

---

[1] The thread was almost completely immersed.

The Density of the Mixed Vapors.—Since it thus appeared that the densities of the substances, when separate, were normal, it followed that the main divergence was due to some factor affecting the vapor pressure of the mixture, and such as to make the observed value nearly 4 per cent. lower than the calculated value. It seemed possible that, although the substances when separate showed normal vapor densities, yet when mixed they might influence one another so as to cause the mixture to have an abnormally high density, and therefore an abnormally low vapor pressure The density of the mixed vapors was therefore determind, using the same methods as for calomel, excepting that two bulbs were attached to the flask, one for each substance. As the data are not of permanent value, the details of the experiments and calculations need not be given. It is sufficient to say that the ratio of the densities found and calculated was 1.02, with an accuracy of ±2 per cent. There was therefore no abnormality which could account for the divergence.

The Solubility of Calomel Vapor in Mercury.—There remained the possibility that, in spite of appearances, calomel might be somewhat soluble in mercury at the temperature concerned. If this turned out to be true, the vapor pressure of the mercury in the mixture would be lowered by the influence of the dissolved calomel, and the total vapor pressure of the mixture would be diminished. A lowering of the vapor pressure of the mercury (1335.4 mm. at 390°) by about 50 mm. would account for the divergence observed. A solubility of the chloride of a metal in the metal itself is not known to occur in many instances, but has been established in the case of bismuth trichloride.[1]

A number of preliminary experiments showed that calomel did dissolve in mercury. They showed also that the complete saturation of a mass of mercury by calomel vapor was an exceedingly slow process even at 360-400°, and that the use of small amounts of mercury, of continual agitation by the vibrations of the stirring apparatus, and of 5-6 hours' time were required for the attainment of the maximum, constant values.[2] The apparatus (Fig. 2) consisted of a small bulb (vol. only 1 cc.) containing a weighed portion of mercury (about 0.5 to 1 g.). The calomel in known amount was contained in a small tube, shown in section and front view in Fig. 2, A. and B. After the calomel tube had been introduced,

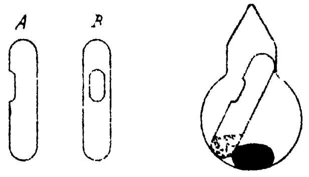


Fig. 2.

---

[1] Eggink, *Z. physik. Chem.*, 64, 449

[2] In the vapor pressure measurements themselves, the fully lowered pressures had been immediately attained This was doubtless due to the fact that the pressures observed proceeded from the fully saturated surface layer of mercury.

the bulb was exhausted to less than 0.1 mm. pressure and sealed. After the charged apparatus had been heated 5–6 hours at the required temperature, it was opened. The loss in weight of the calomel tube gave the quantity dissolved by the mercury, for the weight required to fill the 1 cc. bulb, as vapor, was negligible. At 398°, for example, three observations gave the following results:

Mercury taken. Gram.	Calomel dissolved.	Parts Hg to 1 pt. calom.
1.3118	0.0622	21.1
0.8796	0.0404	21 8
0.4997	0.0237	21.1
	Mean,	21 33

The possibility that the solubility might be reciprocal, and that mercury might dissolve in calomel, was considered. It was observed that the residual calomel, when cold, was perfectly white and showed no evidence of the presence of mercury. In some of the experiments, also, care was taken to use different relative amounts of calomel and of mercury at the same temperature. A little consideration will show that, in such circumstances, if mercury had been appreciably soluble in calomel, constant results for solubilities, calculated as described above, would not have been obtained. It is clear, therefore, that the solubility of mercury vapor in calomel is too slight to require consideration.

For calculation of the lowering in vapor pressure of the mercury, the solubilities must be expressed in numbers of molecules of each substance. If we take HgCl as the formula of the dissolved calomel, the foregoing value at 398° corresponds to 1 mol. HgCl to 25.11 mols. mercury. If, however, the formula is Hg_2Cl_2, then the ratio becomes 1:50.22. If as is conceivable at this high temperature, calomel is unstable, even in solution in mercury, and $HgCl_2$ is the dissolved substance, the ratio is 1:51 22. For reasons which will appear presently, the first ratio was taken.

The solubility was measured at three temperatures. The ratios of molecules of mercury to 1 molecule of HgCl found were as follows: 398°, 25.11; 379°, 26.36; 360°, 39.56. These values were plotted, and the solubilities at even temperatures read from the curve are given in the table following.

The Final Results.—From these experiments it is evident that the partial pressure of mercury vapor in the mixture is not that of pure mercury ($P_{\text{merc.}}$), but that of the solution of calomel in the latter (say $P'_{\text{merc.}}$). For example, at 390°, the value is not 1335.4, but a smaller value. At this temperature the molecular solubility is 1HgCl: 25.4Hg. The partial vapor pressure of mercury over this solution is in proportion to the number of molecules of mercury in the total molecules present; that is to say, it is 1335.4 × 25.4 ÷ 26.4, or 1284.8 mm. Substituting this value for $P_{\text{merc.}}$ in equation 3, we obtain $(^1/_2\,906)^2 \div 1284.8$ = partial pressure of mercuric chloride in the mixture = 159.7. This value, plus the vapor pressure of the mercury as lowered by calomel should equal the observed pressure of the mixture: 159.7 + 1284.8 = 1444.5. The observed pressure of the mixture at this temperature was 1441.4. When the number of measurements involved in the former of these numbers, and the difficulties connected with making exact vapor pressure determinations are taken into account. it will be seen that this agreement within 3.1 mm. in a total of 1444 mm. is much closer than there was any reason to expect. At the other temperatures the degree of agreement is of the same order. It is evident, therefore, that the complete dissociation of calomel vapor, and the absence of HgCl from the vapor, the assumptions underlying equation 3, are satisfactorily established.

The following table contains the complete data. Column 7 shows the vapor pressures of the mixture as calculated by equation 3 from the vapor pressures of calomel (col. 5), and of mercury (col. 4), the latter as depressed by dissolved calomel. Column 8 contains the observed vapor pressures of the mixture. Column 9 gives the differences between the calculated and observed values. The greatest divergence is 6.8, the smallest 0.4, the sum is —0.9, and the deviation of the observations as a whole from the calculated values is only —0.1 mm. It will be noted that, within the range of temperatures covered, the pressure of the mixture has more than doubled itself, but the divergencies show no tendency to progressive change. The average divergence is less than 1 part in 12000. This excellent agreement with the theory that only Hg and $HgCl_2$ are present in the vapor of calomel demonstrates conclusively, within the limits of error of the method, the complete absence alike of HgCl and of Hg_2Cl_2 from the saturated vapor:

1 t	2 Sol'ty $\frac{\text{mols. Hg}}{\text{1 mol. HgCl.}}$	3 $P_{\text{merc.}}$	4 $P'_{\text{merc.}}$, dep by calom.	5 $P_{\text{calom.}}$	6 $p'_{\text{corros.}}$ calc	7 P_{mixt}, calc. 4+6	8 P_{mixt}, obsd.	9 Divergence 8-7
360	39.6	802.6	782.8	434	60.1	843.0	843.6	0.6
365	32.6	876.7	850.6	491	70.9	921.5	924.9	3.4
370	29.3	956.2	924.7	556	83.6	1008.3	1013.0	4.7
375	27.3	1041.6	1004.8	630	98.7	1103.6	1108.4	4.9
380	26.2	1133.0	1091.4	712	116.1	1207.5	1211.1	3.6
385	25.6	1230.9	1184.6	805	136.8	1321.3	1321.7	0.4
390	25.4	1335.4	1284.8	906	159.7	1444.5	1441.4	—3.4
395	25.2	1447.0	1391.8	1017	185.8	1577.6	1570.8	6.8
400	25.1	1566.1	1506.1	1135	213.9	1719.9	1713.4	—6.5

Calculation of the partial pressures of HgCl, by means of equation 4, leads, of course, to the same conclusion. The values found vary on each side of zero, being for the nine temperatures, 0.9, 4.8, 6.8, 7.0, 5.3, 0.5, —5.3, —10.7, and —10.5 mm. The average of the nine is —0.13

mm., and differs therefore from zero by much less than the errors of measurement.

Results with a Mercury Thermometer.—As the platinum resistance thermometer is a difficult instrument to handle, and is not always available, it is worth while to show that the problem might have been solved and the same conclusion reached with the simplest apparatus. With a good nitrogen-filled thermometer, the actual values of the temperatures between 360 and 400° (and the corresponding pressures) are not exceedingly accurate, as, in spite of careful correction, the individual temperatures taken with such a thermometer may be in error as much as ±1°. But when, as in this case, the same thermometer and the same conditions are used in each of the three series of vapor pressure measurements, the errors partly cancel one another and the results may be useful in spite of them.

In the preliminary experiments, the vapor pressures of mercury, calomel, and the mixture had been determind between 360 and 395° with such a thermometer. The simple, submerged bulblet, vapor pressure apparatus[1] was employed, with a good gage. The solubility measurements given above were the only parts of the better data used in the calculation of the results. The individual values of the pressures, being less accurate, need not be given. The greatest divergence in the final results between theory and calculation was 6 mm. and the smallest 1 mm. The average divergence of the results as a whole from the theory of complete dissociation was only −3.3 mm. Problems of this kind can therefore be solved even by the use of the submerged bulblet apparatus and a mercury thermometer.

The Molecular Weight of Calomel in Solution in Mercury.—In the discussion of the theory of the method it was pointed out that three independent observations were required to demonstrate the constitution of calomel vapor. It turned out, however, that the dimensions of the molecular weight of calomel in solution in mercury was an additional unknown quantity, the presence of which, as a part of the problem, was not foreseen. At least one more independent observation is therefore logically necessary to establish the fact that the dissolved calomel is monomolecular. It will be noted, however, that instead of only three observations, three groups of observations, covering a wide range of pressures, were made. The experimental material is therefore amply sufficient to sustain this additional conclusion.

If we assume, for the moment, that the dissolved calomel is bimolecular (Hg_2Cl_2), the ratios of molecules of mercury to molecules of calomel (col. 2) are all doubled. This alters the proportions of mercury molecules to total molecules (*e. g.*, at 390° to 50.8:51.8), and therefore the calculated partial pressures of the mercury in the solution. Figuring on this basis, the final divergencies between calculated and observed data (col. 9) now become —12.2, —9.7, —11.1, —13.5, —18.0, etc., up to —36.6 at 400°. The excellent correspondence thus disappears, and the divergencies increase rapidly with ascending temperature.

---

[1] THIS JOURNAL, 32, 907. It is worth noting that this method is dynamic, while the one used in the main series was static.

Conclusions.—1. A series of vapor pressures of calomel from 360 to 400° has been obtained. The boiling point is found to be 382.5°.

2. It has been shown by a quantitative vapor pressure method (static), that calomel vapor, even when saturated, is wholly dissociated, and that molecules of the classes HgCl and Hg_2Cl_2 are not present.

3. Independent measurements, with an apparatus working on the dynamic principle, lead to the same conclusion.

4. It has been shown that the molecular weight of calomel dissolved in mercury at 360–400° corresponds to the monomolecular formula, HgCl.

5. It has been shown that, by the use of the isoteniscope, chemical problems can be investigated, and results can be obtained, possessing the same order of accuracy that is claimed for the most refined methods of quantitative analysis.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 60.]

TRANSFERENCE EXPERIMENTS WITH THALLOUS SULPHATE AND LEAD NITRATE.

BY K. GEORGE FALK.

Received September 28, 1910.

CONTENTS.—1. Introduction. 2. Apparatus. 3. Description of the Experiments with Thallous Sulphate. 4. The Transference Data for Thallous Sulphate. 5. Description of the Experiments with Lead Nitrate. 6. The Transference Data for Lead Nitrate. 7. Discussion of the Results. 8. Summary.

1. Introduction.

In a paper published some years ago, A. A. Noyes[1] pointed out that the change of the transference number of tri-ionic salts with the concentration might be expected to throw light on the question as to whether intermediate ions, such as KSO_4^- in the case of potassium sulphate, or NO_3Ba^+ in the case of barium nitrate, existed in appreciable quantities in solutions of such salts. Results for potassium sulphate, barium chloride, and barium nitrate were published. In this paper, the results obtained with two other salts of this type, thallous sulphate and lead nitrate, will be given; and the theoretical significance of the transference results will be considered.

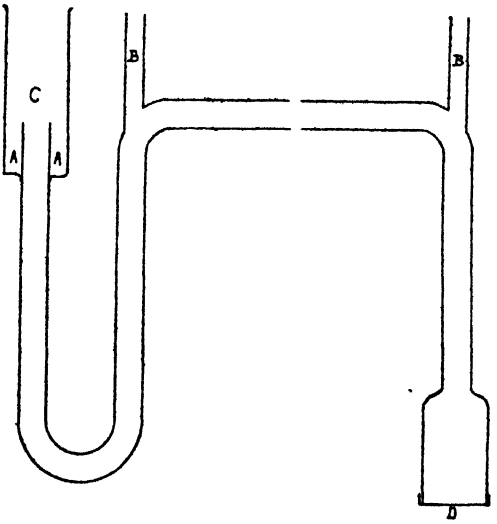
[1] THIS JOURNAL, 23, 37 (1901).

This investigation was undertaken at the suggestion of Prof. A. A. Noyes, and was carried out with the aid of a grant made to him by the Carnegie Institution of Washington.

2. Apparatus.[1]

A cross section of the apparatus, drawn to scale but reduced to 1/5 its natural size, is shown in the accompanying sketch.

The U tube served as the cathode side. The cathode itself rested in the annular space AA in the compartment C. It consisted of an annular strip of sheet platinum fused to a platinum wire, which in turn was fused into a piece of small glass tubing containing mercury, which passed through a rubber stopper closing that side of the apparatus. The diameter of the glass tube throughout the apparatus was 1.5 cm., except at the electrodes, where it was widened to 3.5 cm.



The anode part consisted of the straight tube with the side arm. The widened part at the lower end was closed by fitting over it a gold cup, D. Gold was used instead of platinum because it was easier to work into shape and gave a closer fit. Ceresin was poured in between the upper edge of the cup and the glass, and the joint was covered with two layers of rubber tubing securely wired on. The bottom of the cup was insulated from the bath by a large rubber stopper held up against it by the rubber tubing, which extended sufficiently far down for this purpose. Electric connection with the bottom of the cup was made by a small sheet of platinum pressed against it and fused to a platinum wire which passed through a glass tube in the stopper. The platinum wire was connected below to a copper wire, which was enclosed in black rubber tubing and led up through the bath.

The cathode and anode parts of the apparatus were joined by a double layer of rubber tubing wired in several places and covered with ceresin.

---

[1] To Mr. A. C. Melcher, who rendered valuable assistance in the preparation of the apparatus and development of the experimental method, the writer desires to express his indebtedness.

The two parts were brought so near together that there was practically no free space betwen the glass.

The tubes BB, 1 cm. in diameter, served to introduce or remove the solutions.

The current was taken from the 110-volt city circuit with a sufficient number of 32-candle power 220-volt lamps in series to give the strength of current desired, as shown by a milliammeter placed in series with the apparatus.

The current was measured accurately by means of two silver coulometers, each consisting of a platinum dish 7 cm. in diameter as cathode, a silver disk riveted through its center to a silver rod and wrapped in filter paper as anode, and a 15 per cent. silver nitrate solution as electrolyte. The two coulometers were introduced into the circuit at opposite ends of the transference apparatus, thus guarding against error from leakage of electricity.

3. Description of the Experiments with Thallous Sulphate.

In carrying out the experimental determinations of the transference number of thallous sulphate, a current of electricity was passed through the solution of this salt for a certain length of time, using a definit weight of thallium as anode and allowing thallium to be deposited on the platinum plate at the cathode. The thallium at the two electrodes was dissolved after the experiment and added to the respective electrode solutions; and these were then analyzed. The middle portions were also analyzed, in order to determin whether the changes in concentration extended into them. In this way a theoretically perfect method was attained; for only thallous sulphate was present in the solution, even in the neighborhood of the electrodes; and both the electrode portions, as well as all the middle portions, were analyzed.

The detailed description of the experiments may for convenience be divided into four parts: (1) preparation of the solution; (2) preparation of the anode; (3) electrolysis of the solution and removal of the portions; and (4) analysis of the portions.

Preparation of the Solution.—Kahlbaum's thallous sulphate was used. Though it apparently contained no impurity, it was crystallized from conductivity water. The solutions were made up approximately 0.1 and 0.03 normal with conductivity water, and the exact strength determined gravimetrically as described below. The average of four or five results was adopted as the content of each solution. The solutions used were tested repeatedly with litmus and found to be neutral; and a 0.02 normal solution was more accurately tested with rosolic acid, showing that the solution was no more acid than the water used in preparing it.[1]

---

[1] Reference is made to this fact since Denham (*J. Chem. Soc.*, 93, 59 (1908)) states that his thallous sulphate solution was acid and was largely hydrolyzed.

Preparation of the Anode.—The anode was prepared by depositing electrolytically an accurately known weight of thallium in the gold cup. The procedure differed slightly for the 0 1 and 0 03 normal solutions. In the former case, about thirty grams of the thallous sulphate solution, the exact amount being immaterial, were poured into the anode compartment; about 1 3 grams (accurately weighed) of dilute sulphuric acid were added; and the solution was electrolyzed, with the gold cup as cathode and a small platinum wire as anode, for about 2 hours with a current of 0 030 to 0.040 amperes. Metallic thallium deposited on the cup, and oxygen was evolved at the platinum wire; but at the same time a very small amount of thallic hydroxide deposited on the latter. The presence of the sulphuric acid prevents the formation of all but a minute quantity of thallic hydroxide, whereas the addition of a considerably larger quantity of sulphuric acid would prevent the deposition of metallic thallium. After a sufficient quantity (about 0 5 gram) of thallium had been deposited, the solution was drawn by suction directly into a weighed flask, the platinum wire and the apparatus containing the deposited thallium were washed three times with successive portions of the original solution, and the washings were transformed to the weighed flask. This was then weighed; and the thallium in the solution was determined, after dividing the liquid into two portions so as to obtain check results. By subtracting this weight of thallium from that originally associated with the quantity of water[1] present in the analyzed solution, the quantity of thallium deposited on the gold cup could be accurately determined (within 0 1 mg.).

For the 0.03 normal solution, some slight modifications were necessary. About 40 to 50 grams of the original solution were used for electrolysis and no sulphuric acid was added, since not enough thallic hydroxide formed to interfere with the experiment. The electrolysis was continued only for an hour, as the solution then became exhausted and hydrogen began to be evolved. Duplicate analyses were not made, as there was not enough thallium present in the solution to permit of it. The thallium deposited amounted to about 0 2 gram.

Electrolysis of the Solution.—After the preparation of the thallium deposit on the anode, the apparatus was charged with the solution so that the cathode compartment, C, was filled to three-fifths of its height, air bubbles in the horizontal portion were dislodged, and the apparatus placed in a thermostat at 25°, only the upper ends (two centimeters) of the tubes BB and of the cathode tube being above the surface of the water. The tubes were closed with rubber stoppers, and electric connection was made with the cathode by the column of mercury contained in the glass tube.[1]

---

[1] This quantity of water was calculated by subtracting from the weight of the analyzed solution that of the thallous sulphate found to be present in it, that of the dilute sulphuric acid added, and that of the SO_3 produced by the electrolysis (according to the reaction $Tl_2SO_4 = Tl + 1/2O_2 + SO_3$). The last quantity was calculated from the weight of thallium deposited, after this had been found approximately by a preliminary computation.

The apparatus was allowed to remain in the thermostat long enough to attain its temperature (25°) before starting the current. The electrolysis was continued for three hours or somewhat longer. The approximate strength of the current (as shown by the milliammeter) for the more concentrated solution was 0 012 amperes in the first experiment and 0 015 in the second; for the dilute solution in all three experiments, 0 007 amperes. During the electrolysis no bubbles of gas were evolved at either electrode; and at the end of it the electrode portions were both neutral to litmus.

At the end of the electrolysis the stoppers in the tubes BB were taken out, and the middle portions were drawn out by suction through glass tubes bent at two right angles directly into weighed flasks. In the experiments with the more concentrated solution three middle portions were taken, one consisting of the liquid contained in the horizontal part of the apparatus, one of the liquid in the vertical arm of the cathode side of the apparatus down to the bend, and one of the liquid in the vertical part of the anode side of the apparatus down to one centimeter above the anode compartment. These solutions were weighed and analyzed. In the experiments with the more dilute solution, two middle portions were taken, one consisting of the liquid in the horizontal part and in the upper half of the vertical arm on the anode side, the other of the liquid in the vertical arm on the cathode side down to the bend.

After the removal of the middle portions, the apparatus was taken from the thermostat, and the two parts were disconnected and closed by stoppers. After being dried on the outside the two parts were weighed separately to the nearest centigram

The cathode portion was poured into a flask, and the apparatus washed several times with water, the washings being added to the flask. The thallium deposited on the cathode was dissolved in sulphuric acid and this solution united with the other. Duplicate determinations of the thallium present in known fractional parts of this solution were then made. The apparatus was dried and weighed, together with the stoppers and cathode, so as to obtain the total weight of the cathode portion before it was diluted (including the deposited thallium). The weight of water present in the cathode portion was calculated by subtracting from its total weight that of the thallium[1] and thallous sulphate. From this the amount of thallium in the original solution associated with this quantity of water could be found, whereby the amount of thallium transferred by the current became known.

---

[1] Attempts were made to use as cathode mercury containing a very small quantity of zinc, as recommended by Morden (THIS JOURNAL, 31, 1045 (1909)), but it was found that the zinc rapidly replaced the thallium in the aqueous solution.

With the anode portion, the procedure was similar. After weighing the part of the apparatus containing it, the solution was poured into a flask, the thallium remaining on the anode was dissolved in sulphuric acid either directly or by passing a current through the solution with the cup as anode, and this solution, as well as the water used to rinse the apparatus, was added to the flask and duplicate analyses of known fractions of this solution were made. The anode part of the apparatus was dried and weighed, thus giving the weight of the anode solution plus the thallium remaining on the anode. Assuming the thallium to dissolve according to Faraday's law, and knowing the amount of thallium deposited on the anode originally, the weight of water in the anode portion was calculated, and from that the amount of thallium which originally was present in the solution and on the anode and also the amount of it transferred was determined.

Analysis of the Solutions.—The method of analysis employed was in all cases the determination of the thallium by precipitating and weighing it as thallous iodide. The original solution and the middle portions when analyzed were perfectly neutral toward litmus; the electrode portions had been made acid with dilute sulphuric acid. To the latter, to provide for any oxidation to the thallic state that might have occurred, a few cubic centimeters of a 5 per cent. potassium sulphite solution were added before the precipitation. The solution of thallous sulphate was heated to boiling and a 5 to 10 per cent. solution of potassium iodide, also heated to boiling, was added with stirring. Sufficient iodide was added so that the solution, after precipitation, contained two per cent. or more of potassium iodide. The solution was then boiled vigorously for about a minute, so as to break up the lumps of thallous iodide and enable it to be filtered and washed more readily. The iodide as first precipitated was orange in color, but very soon became light yellow. The solution was allowed to stand overnight, the precipitate collected on a platinum Gooch crucible, washed with about 100 cc. of a 2 per cent. potassium iodide solution until free from sulphate and then with 80 per cent. alcohol to remove the potassium iodide. The precipitates were heated at 160° for an hour, which, as preliminary experiments proved, was sufficient to ensure a perfectly constant weight.

Duplicate analyses in almost all the cases checked within 0.1 per cent., and the method of analysis may therefore be considered accurate to that degree. The presence of sulphuric acid up to the amount used had no apparent influence. The amount of thallous iodide weighed was between 0.3 and 1.2 grams.

---

[1] In making this correction the thallium deposited was assumed to be equivalent to the silver precipitated in the coulometers.

4. The Transference Data for Thallous Sulphate.

The experimental data are given in Tables I and II. The headings are sufficiently explanatory, or become so when considered in connection with the description given above. The letters in the second column have the following significance: PA, Solution from which the thallium was deposited in preparing the anode. A, Anode solution. M_A, Middle portion adjoining the anode solution. M, Middle portion. M_C, Middle portion adjoining the cathode solution. C, Cathode solution. In the case of the 0 02999 normal solution there were only two middle portions, which are designated M_A and M_C, respectively. The changes

TABLE I.—TRANSFERENCE DATA FOR 0 09972 NORMAL THALLOUS SULPHATE SOLUTION AT 25°.*

(Containing 100 11 milli-equivalents of Tl_2SO_4 per 1000 grams of water.[1])

Expt. No.	Portion.	Wt of portion (− Tl).	Wt. of Tl_2SO_4 in portion.	Calc. wt of water in portion.	Milli-equivalents Tl_2SO_4. After electrolysis.	Before electrolysis	Change by electrolysis.	Ag in g and milli-equiv.	Transference number for cation.
1	PA	63.93[2]	1 0651 1 0621	62 75	4 220	6 285	2 065		
	A	64.36	1 9331 1 9311	62 46	7 666	6 252	−0 651	0.1472 g. 1 3645 m e.	0 477
	M_A	19 87	0 4890	19 38	1 940	1 940	0		
	M	32 78	0 8073	31 97	3 203	3.200	+0 003		
	M_C	29 24	0 7197	28 52	2 855	2 855	0		
	C	87.98	2 3260 2.3273	85 72	9 2315	8 5804	+0 651	0 1472 g. 1 3645 m.e.	0 477
2	PA	59 63[3]	0 8634	58 67	3 426	5 873	2 447		
	A	62.58	1 9391 1 9397	60 67	7 695	6 073	−0 825	0 1856 g. 1.720 m.e.	0.479
	M_A	25 90	0 6377	25 26	2.530	2.5285	+0 0015		
	M	28 36	0 6981	27 66	2.770	2.769	+0.001		
	M_C	30.22	0.7440	29 48	2.952	2 951	+0 001		
	C	84 04	2.2681 2 2706	81.85	9 004	8 193	+0.811	0.1855 g. 1 720 m.e.	0 472

[1] The data upon which this value is based are as follows:

Wt. of solution analyzed..	18.00	20.61	34.02	32.22	30 16
Wt of TlI obtained.	0.5817	0 6662	1 0992	1.0406	0 9750
Milli-equiv. Tl per 1000 g. water..................	100 11	100.16	100.11	100.05	100 15

[2] Not including 1.29 grams H_2SO_4 added.

[3] Not including 1.39 grams H_2SO_4 added.

in concentration in the portions adjoining the electrode portions were in all cases within the experimental error of the analyses, and they have therefore not been included in the changes in concentration of the electrode portions.

A number of experiments were made which were faulty in one respect or another; for example, because of a leak of the current between the coulometers, or of unsatisfactory preparation of the thallium deposit on the anode. None of these experiments are reproduced here; but all of those are included in which from external evidence alone, without considering the results, the process appeared to be successful.

TABLE II.—TRANSFERENCE DATA FOR 0 02999 NORMAL THALLOUS SULPHATE SOLUTION AT 25° *

(Containing 30 08 milli-equivalents of Tl_2SO_4 per 1000 grams of water [1])

Expt. No.	Portion.	Wt of portion (+Tl)	Wt of Tl_2SO_4 in portion.	Calc. wt. of water in portion.	Milli-equivalents Tl_2SO_4.			Ag in g. and milli-equiv.	Transference number for cation
					After electrolysis	Before electrolysis.	Change by electrolysis.		
3	PA	83 20	0 3711	82 79	1 4723	2 4904	1 0181		
	A	69 55	0 6792 0 6797	68 88	2 6960	2 0719	-0 3940	0 0891 g. 0 8259 m.e.	0 477
	M_A	47.02	0 3541	46 67	1 4049	1 4038	+0 0011		
	M_C	36.24	0 2724	35 97	1 0804	1 0820	– 0 0016		
	C	86 10	0 7466 0 7460	85 39	2 9612	2 5685	+0 3927	0 0891 g. 0 8259 m e.	0 476
4	PA	86 66	0 3639	86 25	1 4439	2 5944	1 1505		
	A	68 42	0 7012 0 7014	67 73	2 7825	2 0373	–0 4053	0 0909 g. 0 8426 m e.	0 481
	M_A	43 66	0 3288	43 33	1 3045	1 3034	+0 0011		
	M_C	43 36	0 3264	43 03	1 2952	1 2943	+0 00009		
	C	79.31	0 6976 0 6988	78 65	2 7702	2.3658	+0 4044	0 0909 g. 0 8426 m.e	0 480
5	PA	98 33	0.4766	97 81	1.8908	2 9421	1.0513		
	A	68.61	0.6804 0 6814	67 94	2 7016	2 0437	–0 3934	0 0875 g 0 8111 m e	0 485
	M_A	36 23	0 2730	35 96	1 0833	1 0817	+0 0016		
	M_C	43 24	0 3254	42 91	1 2909	1 2907	+0 0002		
	C	92.03	0 7890 0 7904	91 28	3 1333	2 7457	+0 3876	0 0875 g 0 8111 m.e.	0.478

[1] The data upon which this value is based are as follows:

Wt of solution analyzed .	50 26	50.30	46 07	54 16
Wt. of TlI obtained	0.4972	0 4969	0.4547	0 5348
Milli-equiv. Tl. per 1000 g. water.	30.12	30 08	30 05	30.07

Mr. F. L. Hunt working in this laboratory found d_4^{25} = 1.0204 for a solution containing 0.1 equivalent of thallous sulphate in 1 liter solution.

The values of the transference numbers are summarized in Table III. Since there seems to be no error in the method that would tend to make the results at either electrode either too high or too low, and since there was less manipulation involved in the treatment of the cathode than of the anode portion, it seems best to derive the final values of the transference number by taking the mean of the cathode and anode results with double weight assigned to the former. Taking into consideration the variation of the cathode and anode results and the fact that almost all errors are likely to affect them in opposite directions, it seems very improbable that the final values are in error by more than 0.5 per cent.

TABLE III.—SUMMARY OF THE CATION TRANSFERENCE NUMBERS FOR THALLOUS SULPHATE AT 25°.

	0.09972 normal.			0.02999 normal.	
	Cathode.	**Anode.**		**Cathode.**	**Anode.**
	0.477	0.477		0.476	0.477
	0.472	0.479		0.480	0.481
				0.478	0.485
Mean,	0.4745	0.4780	Mean,	0.4780	0.4810
Final value,		0.4757	Final value,		0.4790

Only one value of the transference number of thallous sulphate is recorded in the literature, that of Bein,[1] who obtained the value 0.472 for the transference number of the cation at 23° at the concentration 0.052 normal.

---

[1] *Z physik Chem*, 27, 46 (1898)

* See heading of Tables I and II The Analytical Data from which the values in Tables I and II were derived are as follows

Expt. No.		P.A.		A.		M_A.	M.	M_C.	C	
1	Fraction analyzed.	$\frac{43.66}{79.39}$	$\frac{35.73}{79.39}$	$\frac{53.76}{218.35}$	$\frac{38.17}{218.35}$	Whole	Whole	Whole	$\frac{50.92}{252.62}$	$\frac{53.39}{252.62}$
	Grams TlI	0.7690	0.6276	0.6250	0.4433	0.6421	1.0599	0.9449	0.6156	0.6458
2	Fraction analyzed	Whole		$\frac{49.49}{182.32}$	$\frac{59.28}{182.32}$	Whole	Whole	Whole	$\frac{63.17}{260.83}$	$\frac{58.31}{260.83}$
	Grams TlI .	1.1336		0.6911	0.8280	0.8373	0.9166	0.9769	0.7212	0.6665
3	Fraction analyzed	Whole		$\frac{79.60}{164.86}$	$\frac{84.27}{164.86}$	Whole		Whole	$\frac{75.82}{232.78}$	$\frac{75.62}{232.78}$
	Grams TlI	0.4872		0.4306	0.4562	0.4649		0.3576	0.3193	0.3182
4	Fraction analyzed	Whole		$\frac{74.26}{158.87}$	$\frac{83.58}{158.87}$	Whole		Whole	$\frac{73.07}{210.34}$	$\frac{72.24}{210.34}$
	Grams TlI	0.4778		0.4303	0.4845	0.4317		0.4286	0.3182	0.3151
5	Fraction analyzed .	Whole		$\frac{71.04}{152.44}$	$\frac{80.49}{152.44}$	Whole		Whole	$\frac{86.85}{215.03}$	$\frac{88.43}{215.03}$
	Grams TlI..	0.6257		0.4163	0.4724	0.3585		0.4272	0.4194	0.4268

5. Description of the Experiments with Lead Nitrate.

The apparatus which was used in the transference experiments with thallous sulphate was also used in those with lead nitrate. Except for a few modifications which will be described, the experimental method was essentially the same.

Preparation of the Solution.—Kahlbaum's lead nitrate, recrystallized from conductivity water to which 1 per cent. nitric acid had been added, was used. Solutions approximately 0.1 and 0.03 normal were prepared with conductivity water, and the exact contents determined gravimetrically. These solutions showed a neutral reaction.

Preparation of the Anode.—Finely granulated "test lead," such as is used in assaying, was employed in preparing the anode. It was found by analysis to contain 99.83 per cent. lead, with small amounts of oxide and moisture. A known weight was placed in the gold cup of the apparatus before adding the solution.

Electrolysis of the Solution.—The procedure was the same as with thallous sulphate, except that the lead which remained undissolved at the anode after the electrolysis was dissolved in nitric acid and added to the anode solution after the apparatus had been dried and weighed. It is therefore not included in the weights of anode solutions given in the tables. The electrode solutions remained clear during the passage of the current; but after their removal from the apparatus they became cloudy in a few minutes on account of lead hydroxide formed from the finely divided lead and the oxygen of the air. This shows that nitric acid was not formed at either electrode. The weight of lead which dissolved at the anode and separated at the cathode was assumed to be equivalent to the weight of silver separated in the coulometers. The weight of lead used as anode given in the tables is the calculated weight of pure lead (*i. e.*, the weight of the test lead multiplied by 0 9983).

Analysis of the Solutions.—The lead was precipitated and weighed as lead chromate in all cases. In the case of the neutral solutions, 1 cc. of a 10 per cent. sodium acetate solution and 10 cc. of a 5-fold normal acetic acid solution were added, and the hot solution was precipitated with a one or two per cent. potassium dichromate solution, about 50 per cent. in excess of that required for precipitation being employed. The solutions containing the precipitates were allowed to stand at least 12 hours; the lead chromate was then collected on a platinum Gooch crucible, washed with 200 to 300 cc. water, and dried at 160–170°. To the solutions which contained free nitric acid, either an excess of sodium acetate was added (experiments 1–3), or sodium carbonate solution was added until the acid was neutralized (experiments 4–7), and then acetic acid and dichromate were added as before. Duplicate analyses were found to agree much more satisfactorily when the precipitates were amorphous in character and settled slowly, than when they were crystallin and the solutions cleared rapidly, which last was the case when insufficient sodium acetate was added. Duplicate analyses checked within 0.1 per cent. except in case of some of the dilute solutions (experiments 4–7).

6. The Transference Data for Lead Nitrate.

The data and calculated results are given in Tables IV and V. The changes in the middle portions have not been included in the calculated changes of the electrode portions in any case:

TABLE IV.—TRANSFERENCE DATA FOR 0.1002 NORMAL LEAD NITRATE SOLUTION AT 25°.*

(Containing 100.50 milli-equivalents $Pb(NO_3)_2$ per 1000 grams of water.[1])

Expt. No.	Portion.	Wt. of portion (+ Pb).	Wt. of $Pb(NO_3)_2$ in portion.	Calc wt. of water in portion.	Grams and milli-equiv. Pb at anode.[2]	Milli-equiv $Pb(NO_3)_2$. Before electrolysis.	After electrolysis.	Change.	Ag in grams and milli-equiv.	Transference number for cation.
1	A	61.05	1.5829 1.5814	59.94	0.4380 g. 4.230 m.e.	6.024	9.556	—0.698	0.1566 g 1.452 m.e.	0.481
	M_A	23.02	0.3765	22.64		2.275	2.274	—0.001		
	M	33.36	0.5465	32.81		3.298	3.301	+0.003		
	M_C	31.49	0.5155	30.97		3.112	3.114	+0.002		
	C	71.07	1.2803 1.2824	69.88		7.023	7.740	+0.717	0.1567 g 1.452 m.e.	0.494
2	A	61.00	1.5283 1.5290	59.88	0.4087 g. 3.947 m.e.	6.018	9.233	−0.732	0.1602 g. 1.485 m.e.	0.493
	M_A	22.85	0.3745	22.48		2.259	2.262	+0.003		
	M	34.66	0.5678	34.09		3.426	3.429	+0.003		
	M_C	28.14	0.4606	27.68		2.782	3.782	0		
	C	74.49	1.3384 1.3391	73.24		7.361	8.086	+0.725	0.1601 g. 1.484 m.e.	0.488
3	A	62.50	1.4573 1.4591	61.35	0.3514 g. 3.394 m.e.	6.166	8.808	—0.752	0.1658 g. 1.537 m.e.	0.489
	M_A	26.15	0.4274	25.72		2.585	2.581	—0.004		
	M	28.90	0.4739	28.43		2.857	2.862	+0.005		
	M_C	30.86	0.5053	30.35		3.050	3.052	+0.002		
	C	80.64	1.4414 1.4416	79.29		7.969	8.707	+0.738	0.1658 g. 1.537 m.e.	0.480

[1] The data upon which this value is based are as follows:

Wt. of solution analyzed........ ..	27.97	35.95	24.74	24.09
Wt. of $PbCrO_4$ obtained....	0.4467	0.5745	0.3948	0.3847
Milli-equiv. Pb per 1000 g. of water	100.51	100.57	100.44	100.48

[2] Test lead analyses:

Wt. of test lead analyzed....	0.8538	0.8936	0.1444	0.3794	0.6358
Wt. of $PbCrO_4$ obtained.	1.3300	1.3912	0.2244	0.5916	0.9915
Per cent. Pb................	99.85	99.79	99.61	99.92	99.96

TABLE V.—TRANSFERENCE DATA FOR 0 02995 NORMAL LEAD NITRATE SOLUTION AT 25°.*

(Containing 30 04 milli-equivalents of $Pb(NO_3)_2$ per 1000 grams of water.[1])

Expt. No.	Portion.	Wt. of portion (+ Pb.)	Wt. of $Pb(NO_3)_2$ in portion.	Calc wt. of water in portion.	Grams and milli-equiv. Pb at anode.	Milli-equiv. $Pb(NO_3)_2$.			Ag. in grams and milli-equiv.	Transference number for cation.
						Before electrolysis.	After electrolysis.	Change.		
4	A	63.20	0 6205 0 6224	62 84	0 2321 g. 2 2424 m.e	1.8877	3 7535	−0.3766	0 0831 g 0 7703 m e	0 489
	M_A	52 02	0 2577	51 76		1 5549	1.5568	+0 0019		
	M_C	33.88	0 1676	33 71		1 0127	1 0121	—0.0006		
	C	68 52	0 3999 0 4008	68 17		2 0478	2 4180	+0 3702	0 0830 g. 0 7694 m e	0 481
5	A	66.66	0 8558 0 8556	66.27	0 3693 g. 3 5671 m e	1 9908	5 1684	—0 3885	0 0837 g. 0 7759 m e.	0 502
	M_A	48 07	0 2385	47.83		1 4368	1 4404	+0 0036		
	M_C	36.30	0.1791	36 12		1 0850	1.0820	—0 0030		
	C	67 85	0.3986 0 3993	67 50		2 0277	2 4096	+0 3818	0 0837 g. 0 7759 m.e.	0 492
6	A	66.39	0 6326 0 6327	65 98	0.2343 g. 2 2637 m e	1 9820	3.8214	0 4243	0 0959 g 0 8890 m e	0 478
	M_A	50.35	0 2498	50 10		1 5050	1 5085	+0 0035		
	M_C	34.16	0 1686	33 99		1 0210	1 0183	—0 0027		
	C	68 58	0.4110 0 4112	68.22		2.0493	2 4829	+0 4336	0 0958 g 0 8880 m.e.	0 489
7	A	64.79	0 6507 0 6485	64.40	0 2498 g 2 4131 m e.	1 9346	3 9236	0.4251	0 0944 g 0 8750 m e.	0 486
	M_A	48 58	0 2408	48 34		1 4521	1 4547	+0 0026		
	M_C	36 54	0 1805	36 36		1 0923	1 0900	—0 0023		
	C	65 31	0.3931 0 3924	64 96		1 9547	2 3724	+0 4210	0 0944 g. 0.8750 m.e	0 481

[1] The data upon which this value is based are as follows:

Wt. of solution analyzed	48 45	71 36	64 28	48 06
Wt. of $PbCrO_4$ obtained	0 2341	0 3447	0 3101	0 2321
Milli-equiv. Pb per 1000 g of water.	30.057	30.048	30.011	30 044

* See heading of Tables IV and V. The Analytical Data from which the values in Tables IV and V were derived are as follows:

Expt. No.		A.		M_A.	M.	M_C.	C.	
1	Part analyzed	$\frac{47.35}{232.17}$	$\frac{68\ 68}{232.17}$	All	All	All	$\frac{61\ 69}{250.07}$	$\frac{56.65}{250\ 07}$
	Grams $PbCrO_4$	0 3150	0.4565	0 3674	0 5333	0.5030	0.3082	0.2835
2	Part analyzed	$\frac{51.91}{208\ 67}$	$\frac{52.11}{208\ 67}$	All	All	All	$\frac{48\ 88}{210.75}$	$\frac{48.47}{210\ 75}$
	Grams $PbCrO_4$	0 3710	0 3726	0.3654	0 5540	0 4494	0.3029	0 3005
3	Part analyzed	$\frac{56.27}{206.18}$	$\frac{59.26}{206.18}$	All	All	All	$\frac{54.52}{204.53}$	$\frac{56.14}{204.53}$
	Grams $PbCrO_4$	0.3881	0.4092	0.4170	0 4624	0 4931	0.3749	0.3861

(*Continued on bottom of p. 1567.*)

TABLE VI.—SUMMARY OF THE CATION TRANSFERENCE NUMBERS FOR LEAD NITRATE AT 25°.

	0.1002 normal.			0.02994 normal.	
	Cathode.	Anode.		Cathode	Anode.
	0.494	0 481		0 481	0 489
	0.488	0 493		0 492	0 502
	0.480	0 489		0 489	0 478
	----	---		0 481	0.486
Mean,	0 4873	0 4877		---	----
Final value,		0 4875	Mean,	0 4858	0 4889
			Final value,		0 4874

The results are summarized in Table VI. In deriving the final values equal weight has been given to the results obtained from the anode and cathode solutions. It is hardly possible that the error in these final values exceeds ±0 003 or 0 6 per cent.

7. Discussion of the Results.

An examination of the final values given in Tables III and VI shows that for either salt between the concentrations 0 03 and 0.10 normal there is no variation (greater than the probable experimental error) in the transference number of the cation Within this range of concentration the values **0 477** (±0 003) for thallous sulphate, and **0 487** (±0 003) for lead nitrate may therefore be adopted.

It is of interest to compare these values with those at zero concentration which may be calculated from the equivalent conductances of the separate ions. For the ions in question Kohlrausch[1] has derived the following values:

---

[1] *Landolt-Bornstein-Meyerhoffer Tabellen*, p 763 (1905), also *Z Elektrochem.*, **13,** 342 (1907) The values at 25° have been calculated with the aid of Kohlrausch's temperature coefficients A partially independent determination of Λ_{Tl} and Λ_{SO_4} from new data upon the conductance of potassium sulphate and thallous sulphate at 18° and 25° recently obtained in this laboratory has led to the following values at 25°: $\Lambda_{Tl} = 76\ 0$ and $\Lambda_{SO_4} = 80\ 0$ These are seen to be closely concordant with those of Kohlrausch

(*Continued from p. 1560.*)

Expt. No.		A		M_A	M.	M_C	C.	
4	Part analyzed	70 05 197 82	65 05 197 82	All		All	62 30 225 07	75 68 225 07
	Grams $PbCrO_4$	0 2144	0 1997	0 2515		0 1635	0 1080	0 1315
5	Part analyzed	83 10 184 65	75 00 184 65	All		All	89 26 190 42	82 35 190 42
	Grams $PbCrO_4$	0 3758	0 3391	0 2327		0 1748	0 1823	0 1685
6	Part analyzed.	75 62 149 91	73 55 149 91	All		All	66 86 171 55	84 00 171 55
	Grams $PbCrO_4$ . .	0 3114	0 3029	0 2437		0 1645	0 1563	0 1964
7	Part analyzed	69 94 170 40	92 28 170 40	All		All	81 97 155 81	72.63 155.81
	Grams $PbCrO_4$... ...	0.2606	0 3427	0.2350		0.1761	0.2018	0.1785

At 18°: $\Lambda_{Tl} = 66.0$; $\Lambda_{SO_4} = 68.4$; $\Lambda_{Pb} = 61.0$; $\Lambda_{NO_3} = 61.7$.
At 25°: $\Lambda_{Tl} = 75.9$; $\Lambda_{SO_4} = 79.3$; $\Lambda_{Pb} = 71.4$; $\Lambda_{NO_3} = 70.6$.

From these values one obtains for the cation transference number, at 25°, 0.489 for thallous sulphate and 0.503 for lead nitrate. These values are 2.5 and 3.2 per cent., respectively, higher than those directly measured at the higher concentrations. It is not certain whether these differences are real or are due to errors in the values at zero concentration, which are based on extrapolations in the cases of two different types of salts. The fact that there is little, if any, change between 0.10 and 0.03 normal makes it somewhat improbable that there is any considerable change below 0.03 normal.

Assuming that the change is real, it might be due in the case of thallous sulphate to the presence of the intermediate ion $TlSO_4^-$ in the more concentrated solutions. In the case of lead nitrate, on the other hand, the presence of the intermediate ion NO_3Pb^+ would probably cause a change in a direction opposite to that of the observed one.

The effect of the intermediate ion depends, however, on the value of its equivalent conductance, as will be seen from the following values of the transference number for thallium (T_{Tl}) which have been calculated for the two limiting cases, where the only ions present are (1) Tl^+ and $SO_4^{=}$, and (2) Tl^+ and $TlSO_4^-$, by the expressions (1) $T_{Tl} = \Lambda_{Tl}/(\Lambda_{Tl} + \Lambda_{SO_4})$, and (2) $T_{Tl} = (\Lambda_{Tl} - \Lambda_{TlSO_4})/(\Lambda_{Tl} + \Lambda_{TlSO_4})$, for various relative values of Λ_{Tl}, Λ_{SO_4}, and Λ_{TlSO_4}.

	Case (1).	Case (2).
For $\Lambda_{Tl} = \Lambda_{SO_4} = \Lambda_{TlSO_4}$:	$T_{Tl} = 0.50$;	$T_{Tl} = 0.0$.
For $\Lambda_{Tl} = \Lambda_{SO_4} = 2\Lambda_{TlSO_4}$:	$T_{Tl} = 0.50$;	$T_{Tl} = 0.33$.
For $\Lambda_{Tl} = \Lambda_{SO_4} = 3\Lambda_{TlSO_4}$:	$T_{Tl} = 0.50$;	$T_{Tl} = 0.50$.
For $\Lambda_{Tl} = \Lambda_{SO_4} = 4\Lambda_{TlSO_4}$:	$T_{Tl} = 0.50$;	$T_{Tl} = 0.60$.

Identical values would obviously be obtained for the transference number of the nitrate-ion ($T_{NO_3} = 1 - T_{Pb}$) in lead nitrate for the corresponding assumptions that $\Lambda_{Pb} = \Lambda_{NO_3} = 1$ to $4\ \Lambda_{NO_3Pb}$.

These values show that for the case that $\Lambda_{Tl} = \Lambda_{SO_4} = 3\Lambda_{TlSO_4}$ or $\Lambda_{NO_3} = \Lambda_{Pb} = 3\Lambda_{NO_3Pb}$ the presence of the intermediate ion would have no influence on the transference number; and, if it be admitted that the value of Λ_{TlSO_4} or Λ_{NO_3Pb} can be as small as this, no positive conclusion can be drawn from the results. Unfortunately, no direct information is at hand as to the values of these ion-conductances, and they can be estimated only on the basis of kinetic considerations or of analogies with other ions of corresponding molecular complexity. Comparing the $TlSO_4^-$ ion with the $SO_4^{=}$ ion, or the NO_3Pb^+ ion with the Pb^{++} ion, it is evident that, since the electric charge on the former ion is only half as great, the driving force would be only half as great, and that therefore, assuming the ion is of the same size, its velocity and equivalent conductance would also be half as great. If, however, the intermediate ion is formed by direct union of the Tl^+ and SO_4^{--} or the Pb^{++} and NO_3^- ions, it might be expected that the ion would be larger than either of its constituents, so that its equivalent conductance would be less than one-half, and might well be approximately one-third, as great as that of the simpler bivalent ion.[1] It is, on the other hand, not improbable that the union of the simple bivalent and univalent ions to form the univalent intermediate ion is attended with a dehydration, since the relatively small conductance of the simpler bivalent ions indicates that they are, as a rule, more highly hydrated than the univalent ones. If this is the case, the conductance of the intermediate ion might have any value less than that of the constituent univalent ion. Of ions of composition and complexity analogous to $TlSO_4^-$ the hydrosulphate ion (HSO_4^-) and ethyl sulphate ion ($C_2H_5SO_4^-$) seem to deserve especial consideration. For the former, at 25°, Noyes and Stewart[2] have recently concluded that the value lies between 35 and 40, and for the latter Loeb and Nernst[3] found the value 39, while that for $SO_4^=$ is 79.3. Judging from these analogies, the value for $TlSO_4^-$ might also be about one-half that for SO_4.

These statements make clear how the matter stands. The fact that the transference numbers of both thallous sulphate and lead nitrate show little if any change with the concentration up to 0.1 normal does not prove that the intermediate ions of these salts are not present in considerable quantity at the latter concentration, for it is possible that the

---

[1] Prof. G. N. Lewis has suggested the following hypothesis, which requires in the special case here considered that the conductance of the intermediate ion be one-third that of the constituent ions, and which requires in general that the conductance of the intermediate ion has such a value that the transference number would not be influenced by its presence "By the dissociation of a strong electrolyte the typical physical properties (optical, thermal, volume, etc.) suffer no appreciable change. This is also true of the further dissociation of such intermediate ions as KSO_4^-, $BaNO_3^+$, if they exist. It would not, however, be true of such ions as $HC_2O_4^-$ or HSO_4^-, the dissociation of which is attended by a noticeable heat change. The intermediate ions of the former class are probably loose aggregates in which the constituent parts are not in such intimate proximity as to effect their individual properties. It may be assumed, therefore, that their constituents will show the same resistance to motion through the solution as they show when free. Considering now a salt A_2B yielding the ions A^+, B^{--}, and AB^-, whose specific resistances are represented by R_A, B_B, R_{AB}, this assumption requires that $R_{AB} = R_A + R_B$, and that the corresponding mobilities be

$$\Lambda_A = \frac{1}{R_A},\ \Lambda_B = \frac{2}{R_B},\ \text{and}\ \Lambda_{AB} = \frac{1}{R_A + R_B} = \frac{1}{\frac{2}{\Lambda_B} + \frac{1}{\Lambda_A}} = \frac{\Lambda_A\Lambda_B}{2\Lambda_A + \Lambda_B}.$$

This can be shown to be the general condition that the transference number is independent of the amount of intermediate ion. In the special case in which $\Lambda_A = \Lambda_B$, it is obvious that $\Lambda_{AB} = {}^1/_3\Lambda_A$."

[2] THIS JOURNAL, 32, 1142 (1910).

[3] *Z. physik. Chem.*, 2, 962 (1888).

conductance of these ions has such a value as to make the transference numbers independent of the character of the ionization. Unless some general hypothesis, like that suggested by Lewis, can be substantiated, it is somewhat improbable that the conductance should have this unique value, which is less than that for other univalent ions of similar complexity, in the case of any one salt; and it becomes more improbable that this should be true in the case of a number of different salts. Yet this investigation and the previous one[1] made in this laboratory have shown that four different tri-ionic salts, potassium sulphate, thallous sulphate, barium nitrate, and lead nitrate, all show the same substantial constancy of the transference numbers up to a moderate concentration.[2] Some degree of probability therefore attaches to the hypothesis that such tri-ionic salts do not as a rule give rise to intermediate ions, at any rate in quantity exceeding a few per cent. at 0.1-0.2 normal; but that they dissociate directly into three ions. At any rate the statement can be made with positiveness that the transference relations of these tri-ionic salts afford no indication of the presence of intermediate ions; but whether this is due to the non existence of such ions or to the fact that they have a conductance of such magnitude as not to influence the transference cannot be definitely stated.

8. Summary.

In this paper have been described transference experiments with 0.03 and 0.1 normal solutions of thallous sulphate and lead nitrate at 25°. The cation transference numbers found for the thallous salt are **0.479** at 0.03, and **0.476** at 0.1 normal, and for the lead salt **0.487** at both concentrations. The changes in content at both electrodes and in the middle portions have been determind, thus fixing the limit of error in the results, which can hardly exceed ±0.003, or about 0.5 per cent. The transference number at zero concentration as calculated from Kohlrausch's extrapolated values of the equivalent conductances of the separate ions is 0.489 for thallous sulphate and 0.503 for lead nitrate; thus 2.5 to 3.2 per cent. higher than the values found by direct measurement at 0.03-0.10 normal. Whether this change of the transference number with the concentration is real, is uncertain. Even if real, it is small, and lies in the case of thallous sulphate in the direction probably required by the presence of the intermediate ion; in the case of lead nitrate, in the opposit direction. The theoretical bearing of the results is discussed in the last two paragraphs of the preceding section. Taking also into consideration other accurate transference values for tri-ionic salts previously determined, it has been there shown that transference experiments make necessary one of two alternative conclusions: either the intermediate ion is not formed in any considerable proportion by the dissociation of tri-ionic salts up to moderate concentrations (0.1 to 0.2 normal), or else, if it is formed, its equivalent conductance has a definit value of such magnitude that the transference number is independent of its concentration.

---

[1] A. A. Noyes, *Ibid.*, 36, 79 (1901).

[2] Almost all the other tri ionic salts that have been accurately investigated are halides, the transference numbers of which as a rule change considerably with the concentration in a direction opposite to that which the presence of the intermediate ion would require, an effect which is not improbably due to the presence of complex anions. The existing data will be more fully considered with reference to the question here under discussion in a critical review of the results of transference experiments now under preparation.

BOSTON, September, 1910.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE CHARACTER OF SILVER DEPOSITS FROM VARIOUS ELECTROLYTES.

BY JOSIAH SIMPSON HUGHES[1] AND JAMES R. WITHROW

Received September 27, 1910.

In some work previously undertaken by one of us it became of interest to know the conditions which would give silver deposits of various properties or characteristics The discussion of this general subject by Bancroft[2] is of great assistance in indicating the variations of conditions which favor satisfactory deposition. The influence of each particular electrolyte on these conditions and the minor details of the deposit characteristics is a matter for experimentation. In this connection Snowdon[3] has gone thoroughly into the deposition of silver from nitric acid and potassium cyanide, using the rotating cathode. Other electrolytes have been used from time to time, especially in electroanalysis.

It was thought therefore that a repetition of some of the earlier work done on the electrolytic determination of silver would not only be helpful in the direction desired but would also be of interest from an analytical view point. The results included here give the outcome of some of these experiments, together with a summary of a series of trials made with new electrolytes.

The same dish cathodes were used that were employed in the work on copper.[4] The anode also was the same except that the diameter of the spiral was 5 cm. in the present case. The current was supplied by storage cells and was measured by Weston, Model 57, switchboard instruments. The ammeter had a range of one ampere and the scale was divided into hundredths. The voltmeter had a range of six volts and the scale was divided into twentieths. All readings given herein are direct instrument readings and are not referred to the "normal density."

---

[1] The major portion of this work is taken from Mr. Hughes' thesis for the M A. degree, Ohio State University.

[2] *J. Physic. Chem.*, **9**, 277.

[3] *Ibid.*, **9**, 399.

[4] THIS JOURNAL, **30**, 381.

During electrolysis the anode was held 2 cm. above the bottom of the dish so that the distance from all parts of the cathode was nearly equal. The total dilution was always 125 cc., giving an estimated effective cathode area of 110 sq. cm. The time factor in the table is not of much importance, because in many cases the experiment ran all night and the silver was doubtless all out some time before the electrolysis was stopped. Sufficient silver nitrate solution was taken in each experiment to give the amount of silver indicated in the table as being present. Ammonium sulphide was used to test the end points. The following is a list of the liquid reagents used, together with their specific gravity in each case: Nitric acid, 1.42; ammonium hydroxide, 0.90; sulphuric acid, 1.84; perchloric acid, 1.12; and hydrofluosilicic acid, 1.06. Normal NaOH solution was used for this reagent. The deposits were washed and dried in the usual manner[1] before weighing. All data here given were obtained without agitating the electrolyte.

Since the early workers gave very few details of their work it is impossible to repeat it exactly. About all one can do in many cases is merely to use the same electrolyte and often the concentration of that is not known.

The first table gives the results obtained in the quantitative examination of electrolytes hitherto in use for various purposes.

The experiments with the nitric acid electrolyte showed that dense deposits cannot be obtained if the voltage is too high. When the voltage was kept lower, however, the deposits were good and of a crystallin nature. This is in agreement with the work of Kuster and von Steinwehr[2] with this electrolyte. Although sponginess is entirely avoided when the voltage is kept below 1.4 volts, yet the silver is deposited so slowly that there is a tendency for the crystals to grow large and become easily detached. Dense adherent deposits can be obtained without much difficulty, however, if the rotating anode is used. With stationary electrodes it was impossible to set the voltage at 1.3 volts, for instance, and expect it to remain there, for with this electrolyte especially it soon begins to rise and thereby passes the point at which discoloration and sponginess appear on the cathode. If the voltage was kept below 1.35 the deposit was smooth and white, finally becoming visibly crystallin. If after such a deposit is well under way, the voltage is raised to 1.5–1.8 volts, the deposit almost instantly darkens and then becomes spongy. If now the voltage is again lowered to 1.3 volts, there is a flash of white as the whole turns this color without even apparently affecting the de-

---

[1] THIS JOURNAL, 30, 382.

[2] *Z. Elektrochemie*, 4, 451.

No.	Ag present. Gram.	Electrolyte.		Current.		Temp. Centigrade.	Time. Hours.	Ag found. Gram.	Deposit characteristics.
		Reagent.	Amount.	Ampere	Volts.				
1	0.2505	HNO_3	4 cc.	0.07	1.5	25°	12.0		Spongy
2	0.0312	HNO_3	3 cc.	0.07	1.5	25°	13.0	0.0315	Spongy
3	0.0312	HNO_3	3 cc.	0.07	1.5	25°	10.0	0.0305	Spongy
4	0.2505	HNO_3	4 cc	0.04-0.001	1.2-1.35	25°	14.0	0.2503	Crystallin
5	0.2505	HNO_3	4 cc.	0.03-0.001	1.1-1.4	25°		0.2506	Crystallin
6	0.2505	NH_4OH $(NH_4)_2SO_4$	5 cc 12 g.	0.05	1.6-2.0	25°			Very spongy
7	0.2505	NH_4OH $(NH_4)_2SO_4$	1 cc 12 g.	0.04	1.4-2.0	25°			Very spongy
8	0.2505	NH_4OH $(NH_4)_2SO_4$	0.5 cc 12 g.	0.04	1.4-1.9	25°			Spongy Anode deposit
9	0.2505	NH_4OH $(NH_4)_2SO_4$	10 cc 12 g	0.03-0.02	1.2-2.0	25°			Spongy
10	0.2505	NH_4OH $(NH_4)_2SO_4$	25 cc 12 g.	0.04-0.001	1.0-1.3	25°	14.0	0.2504	Good, crystallin
11	0.2505	NH_4OH $(NH_4)_2SO_4$	25 cc 12 g.	0.08-0.001	1.0-1.5	55°-65°	7.5	0.2510	Slightly dark
12	0.2505	NH_4OH $(NH_4)_2SO_4$	2 cc 10 g	0.05-0.001	1.0-1.4	65°	7.5	0.2514	Slightly dark
13	0.2505	NH_4OH $(NH_4)_2SO_4$	2 cc. 10 g	0.03-0.001	1.0-1.8	25°	15.0	0.2513	Dark
14	0.2505	NH_4OH $(NH_4)_2SO_4$	1 cc 10 g	0.03-0.001	1.0	25°			Anode deposit
15	0.2505	NH_4OH $(NH_4)_2SO_4$	2 cc 10 g	0.03-0.001	1.0-1.9	60°	8.0	0.2516	Dark
16	0.2505	NH_4OH $(NH_4)_2SO_4$	2 cc 10 g	0.03-0.001	1.0-1.4	60°		0.2508	Not so dark
17	0.2505	NH_4OH $(NH_4)_2HPO_4$	 10 g	0.07-0.002	1.0-1.7	60°-70°	5.0	0.2502	Crystallin
18	0.2505	NH_4OH $(NH_4)_2HPO_4$	3 cc 25 g	0.1-0.001	1.2-1.8	25°	16.0	0.2508	Crystallin
19	0.2505	NH_4OH $Na_4P_2O_7$	5 cc 5 g	0.05-0.002	1.2-1.9	25°	14.0	0.2509	Crystallin
20	0.2505	NH_4OH $Na_4P_2O_7$	10 cc 5 g	0.05-0.001	1.2-1.9	25°	14.0	0.2506	Crystallin
21	0.2505	HNO_3 $NH_4C_2H_3O_2$	5 cc 25 g	0.07-0.001	1.0-1.7	60°	6.0	0.2506	Good, crystallin
22	0.2505	KCN	2 g	0.02-0.03	2.0-2.5	25°	12.0	0.2506	White
23	0.2505	KCN	2 g.	0.07	2.5-3.0	25°	13.0	0.2515	Brownish
24	0.2505	KCN	2 g.	0.07	2.5-3.0	60°	7.0	0.2507	White, good
25	0.2505	KCN	2 g.	0.07	2.5	25°	15.0	0.2514	Slightly dark
26	0.2505	KCN	2 g	0.07	2.5	65°-70°	4.0	0.2504	White

posit in any other way than color. Even the most delicate cauliflower-like effect of some spongy deposits is merely changed from dark (even black) to spotless white. This change is so closely connected with the change in voltage that it suggests its possible utilization in detecting the maximum allowable voltage for useful deposition from electrolytes which show the phenomenon. Nothing further could be done with it, however, at this time.

With the higher voltage much hydrogen is liberated at the cathode. This obviously reduces the cathode area and in this way greatly increases the effective current density. Conditions of this kind would naturally be expected to give rise to poor metallic deposits.

Once upon reducing the voltage in the manner described above, the deposit soon became a mass of needles a half millimeter or more in length.

Then when the voltage was raised to 1.6 volts bubbles of gas collected at once between the needles and did not visibly disengage themselves. This so reduced the cathode surface that only the termination of the needles was the effective cathode. This was shown by the fact that the terminations became like jet and stood out in marked contrast on the white background. Reducing the volts to 1 3 changed these terminations at once to their original white color.

In order to study the black deposit, often obtained, a heavy one was secured. The voltage was then reduced to 1.2 volts. This caused the usual flash of white metallic silver which covered everything that was black just before. The current was then reversed without disturbing anything in the dish. The double layer deposit (as it appeared to be) was now the anode and it almost completely corroded off without changing from the color of the later deposit of silver. That is, the layer of black which was laid down first on the cathode never became visible on what was now the anode. Although this is not definit proof, it seems to indicate that the white flash is a real bleaching or change in color of the black silver itself.

In the work with nitric acid there was often a tendency toward the formation of the well-known black, crystallized deposit on the anode.

Beautiful silvery deposits, difficult to distinguish from the dish, were often obtained at first from the ammonium sulphate-ammonium hydroxide electrolyte. Some of these deposits were like burnished silver but as the deposits became heavier they became more velvet-like and as the voltage ran above 1 4 volts they darkened. Rarely, however, did they develop sponginess as rapidly or to the same extent as those from nitric acid.

Number 9 started well but later became spongy. The 10th result and the beginning of number 9 show the favorable effect of lower voltage than was used at first. Experiments 11 to 16, inclusive, give in each case darkened deposits of varying intensity of shade. All of them were made with higher voltage. Some of them were run at elevated temperature but without any appreciable effect other than the usual corresponding shortening of the time necessary for complete precipitation. The weights of the deposits also in all cases with this electrolyte were high except when the pressure was kept below 1.4 volts. This is in agreement with the experience of Krutwig,[1] who proposed this electrolyte.

On a few occasions, when only a small amount of ammonium hydroxide was used with the ammonium sulphate electrolyte, the first layers of silver which came down were purple in color, changing in places to a deep blue color. This calls to mind at once the blue form of silver made by

---

[1] *Ber.*, 15, 1262.

Carey Lea years ago. Snowdon[1] seems to have encountered this under other circumstances. The deposits here mentioned were not as uniform as Snowdon obtained when he used a colloidal addition agent. None of the deposits made at 1.5 volts were adherent The simultaneous darkening of the deposits and excess weight might be explained by the assumption of the formation of silver sulphide at the cathode. The function of the ammonium hydroxide appears to be the prevention of anodic deposit formation. When the amount of this reagent was lessened there was an anodic deposit as was found in experiments 8 and 14.

When ammonium sulphate was employed in the absence of ammonium hydroxide there very quickly formed on the anode a heavy black deposit which shone at times like polished graphite This deposit was at once dispelled upon the addition of a few drops of ammonium hydroxide.

In experiment 17 sufficient ammonium hydroxide was added to dissolve the precipitate first formed. When the ammoniacal phosphate and pyrophosphate electrolytes were used the deposits were crystallin in every case. Here also, however, too high voltage causes sponginess.

The potassium cyanide used in the experiments with this electrolyte was the commercial grade Most of the deposits from this electrolyte were white and good. The quantitative results seem to be best when an elevated temperature is used The dark effect which appeared in the electrolyte around the anode seemed to migrate to the cathode. There was always a slight black residue left after dissolving the silver deposit in nitric acid This substance resembled carbon and disappeared when the dish was heated but was not identified

The final table shows in a compact way the general results obtained when using other electrolytes than those mentioned in the literature. The experiments are all qualitative and were made to determin the character of the resulting deposits. The fluosilicic acid electrolyte is not new, although given in the final table. It has been used by Jarvis and Kern in their study of the effect of addition agents on the density and coherence of silver deposits[2] This article is only accessible to us through abstract.[3] The abstract gives no information, however, concerning the nature of the deposits obtained from this particular electrolyte. We only examined the electrolyte qualitatively and hence put it with the other qualitative results.

The deposits from sulphuric acid and glycerol were so coarsely crystallin as to be non adherent. The sodium and ammonium hydroxide mixture gave a fairly adherent deposit. The deposit in experiment 8 was not so coarse as in the preceding experiments. The fluosilicic acid seems to be the most satisfactory of any of the last electrolytes tried. At 50° there was no oxide on the anode, and the deposit did not become spongy at as low a voltage as in the other cases.

---

[1] *J Physic. Chem.*, 9, 397.

[2] *School Mines Quart.*, 30, 100

[3] *Chem Abs.*, 3, 1495.

No.	Electrolyte. Reagent.	 Amount.	Current. Ampere.	 Volts	Temp. Centigrade	Anode deposit.	Cathode deposit.
1	H_2SO_4	1–10 cc.			25°	Oxide each time	Coarse, crystallin
2	H_2SO_4 Glycerol	10 cc. 1 cc.	0 05	1.3	25°	None	Coarse, crystallin
3	Same	Same	0 07	1.5	25°	None	Spongy
4	NH_4CNS	5 g	0 05	1.1	25°	Sulphur	Black
5	NaOH NH_4OH	2 cc. 4 cc	0 04	1.1	25°	None	Coarse, crystallin
6	Same	Same	0 08	1.6	25°	None	Spongy
7	NH_4OH $HClO_4$	4 cc. 3 cc	0.05	1.2	25°	Oxide	
8	Same	4 cc. 4 cc.	0.04	1 1	25°	None	Crystallin
9	Same	4 cc. 4 cc.	0.08	1.7	25°	None	Spongy
10	K_2F_2	1–5 g.			25°	Oxide each time	Coarse, crystallin
11	H_2SiF_6	5 cc.	0 08	1.3	25°	Oxide	Coarse, crystallin
12	H_2SiF_6	5 cc.	0.1	1.4	50°		Good
13	H_2SiF_6	5 cc.	0.2	1.7	50°		Spongy

Summary.

1. The general characteristics are described of the silver deposits from a variety of electrolytes.

2. With all the electrolytes tried except cyanide·ly, hc is a point at about 1.4 volts beyond which, with the conditions 'nt a used, spongy deposits will result. With cyanide this point is much higher.

3. Satisfactory conditions have been tabulated for the quantitative precipitation of silver from several electrolytes.

4. Several other electrolytes have been tried which seem worthy of further investigation.

COLUMBUS, OHIO.

RATE OF HYDRATION OF PYROPHOSPHORIC ACID. A CORRECTION.

By G. A. ABBOTT.

Through the kindness of Dr. J. M. Bell, of the University of North Carolina, my attention has recently been called to the fact that the experimental data given in Table IV of my article on the Rate of Hydration of Pyrophosphoric Acid[1] are not consistent with the statement in the text that the specific conductance of a mixture of the pyro and ortho acids is a linear function of its composition. Through a regrettable error in copying, the wrong data were included in the table referred to, and it is the purpose of this note to present the correct ones. The following table should be substituted for that given in the article:

---

[1] THIS JOURNAL, 31, 766 (1909).

TABLE IV.—SPECIFIC CONDUCTANCE (L) $\times 10^6$ OF MIXTURES OF PYRO- AND ORTHO-PHOSPHORIC ACIDS AT 18°.

At wts. P per liter.	Per cent P as ortho acid.	100	75	50	25	0
	Per cent. P as pyro acid.	0	25	50	75	100
0 1	Found	9650	11640	13650	15610	17690
	Calculated	..	11660	13670	15680	. .
0 05	Found	6135	6992	7874	8726	9622
	Calculated..	. .	7007	7878	8750	....
0.01	Found	2030	2154	2275	2388	2517
	Calculated	. ..	2152	2274	2395	.. .

The degree of the divergence from a linear relation between conductance and composition will be seen by comparing the found values with the calculated ones given in the rows just beneath them. These calculated values were obtained by the expression $xL_o + (1 - x)L_p$, where x represents the fraction of the phosphorus present in the mixture as ortho acid, L_o the conductance of the pure ortho acid, and L_p that of the pure pyro acid. It will be seen that the difference is largest in the case of the mixtures with 25 per cent. ortho acid, but that even in this case it averages only about 0 4 per cent.

This opportunity may be also utilized for correcting the following typographical errors in the article on The Ionization Relations of Ortho- and Pyrophosphoric Acids and their Sodium Salts, by Abbott and Bray:[1]

On page 742, line 19, insert K_B in the denominator of the expression for K_3.

On page 751, line 14, read 353 8 instead of 358 8.

On page 751, last two lines, read K'_1, for K'_2 and K'_2 for K'_1.

On page 753, in Fig. 2, read $Na_4P_2O_7$ in place of $Na_4P_4O_3$.

On page 762, in Table XXIII, read $H_2PO_4^-$ in place of HPO_4^- and $H_3P_2O_7^-$ in place of $HP_2O_7^-$.

UNIV. OF NORTH DAKOTA, Oct., 1910.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

A REVISION OF THE ATOMIC WEIGHT OF CALCIUM. I. ANALYSIS OF CALCIUM BROMIDE.

BY THEODORE W. RICHARDS AND OTTO HÖNIGSCHMID.

Received October 24, 1910.

Introduction.

During the last fifty years the atomic weight of calcium has been repeatedly investigated, but most of the investigations have not led to very favorable results. According to the opinion of Brauner,[1] one of the most competent of modern critics, only two of the modern researches, namely that by one of the present authors[2] and that by Hinrichsen,[3] are to be considered as free from serious error.

---

[1] THIS JOURNAL, 31, 729 (1909).

The investigation of the atomic weight of calcium was undertaken at Harvard about fifteen years ago, and preliminary determinations were made upon the relation of calcium chloride to silver chloride, resulting in a value for the atomic weight of calcium of 40.085, if silver and chlorine are given the values of 107.88 and 35.457, respectively. Hinrichsen, on the other hand, without knowledge of the Harvard work, used the old method of converting calcium carbonate to oxide, obtaining therefrom a much higher value, 40.139. Before Stas' atomic weight of silver (107.93) was found to be in error, the two results seemed to be fairly consistent, but with modern values the difference is considerable.

This difference between the two values suggests the importance of a new determination of this important constant, especially because each of the earlier investigators had used only one method. We accordingly began the investigation with the analysis of calcium bromide, and determined not only the amount of silver needed to precipitate the bromine, but also the amount of silver bromide obtained. As will be seen, the results supported rather the earlier Harvard work than the higher value of Hinrichsen, The outcome of this investigation of the bromide (Ca = 40.070) is slightly lower even than the value obtained from the chloride. Further work upon the chloride has already been begun and it is hoped that further results upon this subject also may be communicated in the near future.

It is a pleasure to express our obligation to the Carnegie Institute of Washington for generous pecuniary assistance, without which much of the apparatus necessary in this investigation could not have been procured.

Preparation of Materials.

During the earlier work upon the atomic weight of calcium, undertaken fifteen years ago, certain tests were made concerning the adequacy of the purification of calcium nitrate from magnesium and from allied elements.

A concentrated calcium nitrate solution containing some magnesium was treated with milk of lime, and the solution was allowed to stand for three days, being shaken repeatedly. One-tenth liter of the supernatant solution, containing about 25 grams of calcium nitrate, was diluted to 0.3 liter and made strongly alkaline with ammonia. Fifty grams of ammonium chloride were added and the calcium was wholly precipitated hot by excess of ammonium oxalate. No magnesium whatever could be found by the usual phosphate test in the filtrate, showing that the treatment with lime eliminates most of the magnesium; but the test does not conclusively prove that all the impurity is removed, for a trace might have been carried down with the oxalate, and thus have escaped detection. It will presently be shown that the crystallization of the nitrate is an effective means of removing the last traces of magnesium, if any such are present.

---

[1] Brauner, Abegg's "Handbuch der anorganischen Chemie," II, [2] 175 (1905) [Leipzig].

[2] Richards, THIS JOURNAL, 24, 374 (1902); *Z. anorg Chem.*, 31, 271 (1902); "Experimentelle Untersuchungen," 626 (1909).

[3] Hinrichsen, *Z. physik. Chem.*, 39, 311 (1902); 40, 746 (1902).

Turning now to the removal of barium and strontium from the calcium precipitations, an effort to accomplish this by means of sulphuric acid may first be described First a 20 per cent. solution of calcium nitrate was treated with a small quantity of sulphuric acid, enough to produce a small precipitate, and this precipitate was tested carefully for strontium and barium with negative results The successive addition, three times, of small further weights of sulphuric acid likewise gave no test for strontium or barium, in spite of the fact that the solution was known to contain a precipitable amount of strontium and a trace of barium.

There is indeed nothing surprising in this observation; it is owing to the fact that the solubility of any electrolyte in a solvent containing different ions is so much increased that the last traces cannot be eliminated by any ordinary process of precipitation. In order to eliminate the impurity, the desired substance, not the impurity, must be separated out.

Abandoning now these methods of purification, which rest upon a wrong principle, the following test was made of the recrystallization of calcium nitrate. To 200 grams of a fairly pure sample of calcium nitrate were added 2 grams each of barium, strontium and magnesium nitrates. The mixed solution was then concentrated and about three fourths of the calcium nitrate was crystallized from it by cooling. In the mother liquor strong tests for barium, strontium and magnesium could be obtained, while in the crystals indications of these impurities were much feebler, although still unquestionable. The crystals were dissolved and recrystallized twice. The third mother liquor gave no test whatever for magnesium by means of phosphate solutions in the usual way, or for strontium in the spectroscope, but gave a very faint precipitate with sulphuric acid, showing the presence of barium. The crystals contained much less barium.

It is clear that when the calcium nitrate is recrystallized, these other contaminating nitrates tend strongly toward the mother liquor. Hence it is not surprising that the next crystallization, the fourth, yielded crystals in which no impurity whatsoever could be found by any ordinary tests. If four crystallizations can accomplish this, when as much as three per cent. of impurity is present, it is clear that when the initial purity is greater, the product must be exceedingly pure, especially upon still further crystallization; for in the distribution between the crystals and mother liquor, each mother liquor tends to hold the greater part of the contaminating substance. Hence both in the earlier investigation and in the present one, as well as in any other investigation in which pure calcium salts are needed, it was our invariable practice to purify the material through the recrystallization of the nitrate.

Calcium Nitrate.—For the present investigation 2 kilograms of a good quality of marble were dissolved in a small excess of the purest commercial nitric acid and the solution was boiled with chlorine water in order to oxidize the iron—an end effected only very slowly by dilute nitric acid. Pure milk of lime was then added in slight excess in order to precipitate the iron and magnesium. The clear filtrate, after the separation of the impurities in solid form, was evaporated to crystallization; and the nitrate was crystallized five times in porcelain vessels and yet five times more in platinum vessels. Each crop of crystals was thoroughly freed from mother liquor by means of a centrifugal machine, at first of porcelain, afterwards of platinum, so that the final crystals came in contact with nothing but the noble metal.

A second specimen of calcium nitrate was prepared from pure calcium carbonate which had been precipitated from nitrate prepared in the manner above described, but with fewer crystallizations. The carbonate was precipitated by means of ammonium carbonate and was washed by repeated decantations and centrifugal action. It was finally dissolved in the purest nitric acid and the nitrate was crystallized four times from the purest water in platinum vessels and whirled in the platinum centrifuge. This calcium nitrate (Sample 2) was used as the basis for the preparation of most of the calcium bromide.

Calcium Carbonate.—From the solution of calcium nitrate thus prepared the carbonate was precipitated by means of very pure ammonium carbonate. For the preparation of this substance in a state of sufficient purity, the purest ammonium carbonate of commerce was distilled with water by means of a platinum cooler. The distillate was collected in a platinum flask containing thrice distilled water, cooled with ice outside. The precipitation of the calcium carbonate was conducted at 100° in a platinum vessel and the precipitate was repeatedly washed with the purest water and centrifugally freed from adhering wash water. The pure carbonate was preserved in a platinum dish in a desiccator containing lime made from pure marble, in order to protect it from the access of impurity from glass and from the atmosphere of the laboratory. It is needless to say that carbonates are especially liable to be contaminated by traces of any strong acid in their neighborhood.

Hydrobromic Acid.—This acid, which was used in very large amounts, was made by the catalytic action of hot platinum on the mixture of hydrogen and bromine vapor. The bromine was prepared from a mixture of pure bromide and bromate by means of sulphuric acid and was still further purified before it was united with the hydrogen.

The bromide had been made from bromate, and this had been many times recrystallized in order to free it from traces of chloride and chlorate. The bromate, and therefore the bromide, made from it, were almost, if not quite, free from iodine, as far as any ordinary test could indicate.[1]

The purest concentrated sulphuric acid of the laboratory was used for the decomposition of the mixed bromate and bromide, and the reaction was carried out in a flask, into which was ground a glass stopper containing a drop funnel and the tube for leading off the bromine vapor. The flask was partly filled with a cold saturated solution of potassium bromide, and the calculated weight of the bromate was added in solid condition. The exit tube was led into another flask partially filled with the purest water and packed in ice; and the reaction was carried out by the gradual dropping in of the acid and gentle warming. There was no difficulty in regulating the speed of the reaction in this way. In each operation only about 50 grams of bromine were prepared, but as this was repeated twenty times, about a kilogram was finally obtained. The bromine thus prepared was purified by solution in a concentrated solution of calcium bromide (made from the same bromine and pure halogen-free lime, according to Stas' method) and the pure bromine was finally once more distilled.

From this bromine, hydrobromic acid was made, as already stated, through direct union of the components with catalytic acceleration by means of platinum asbestos. The hydrogen was prepared through the action of so-called "hydrone" (an alloy of lead and sodium) upon water. The gas was passed through a drying apparatus filled with stick potash, next through a gas-washing bottle filled with the pure bromine, and finally into a Jena hard-glass tube in which platinum asbestos was heated by means of an electric furnace to about 400°. The hydrobromic acid was led into pure water and cooled by ice. The dilute solution of hydrobromic acid thus made always contained an excess of bromine; upon distillation, this bromine, together with any possible traces of iodine which might have been present, came over first and was discarded. The main portion of the acid was distilled and condensed by means of a quartz cooler, and the distillate was collected in a quartz flask.

---

[1] These materials were both presented to us by Mr. H. H. Dow, of the Midland Chemical Company, Indiana. We take pleasure in acknowledging our indebtedness to him for his generosity and for the trouble which he took in conducting very carefully the preliminary purification of large amounts of both substances.

Calcium Bromide.—All the calcium bromide used in the investigation was prepared with hydrobromic acid made in this fashion. The pure specimens of calcium carbonate were in the first place heated in an electric oven until wholly dry and free from traces of ammonium salts which always cling to carbonate prepared as this had been. Even if traces of the ammonium salts remained after this treatment, they would not have been harmful; for they must have been wholly volatilized at the high temperature to which the calcium bromide was subsequently heated. Calcium carbonate thus dried was added in small portions to the pure acid in the quartz flask as long as evolution of gas continued. The solution was then slightly acidified, transferred to a quartz dish and concentrated upon an electric stove. The solution always became yellow, because traces of calcium nitrate (held by the calcium carbonate) invariably set free corresponding traces of bromine during the evaporation.

In these quartz vessels the bromide was recrystallized; thus from beginning to end neither the factors nor the product of the reaction came into contact with glass. The first specimen of calcium bromide was nine times crystallized, during which process of course the greater part of the salt found its way into the mother liquors, and only substance enough for two analyses (Nos. 16 and 17) was obtained. The substance from the mother liquors, after four recrystallizations, was used for preliminary determinations.

A second preparation of bromide was made out of the second preparation of nitrate in a similar manner except that the bromide was crystallized only four times. This preparation served for all the final analyses with the exception of the two mentioned above.

Before the final crystallization in each case the solution was filtered through a platinum Gooch-Munroe crucible. This is important, for in spite of the greatest possible care traces of dust find their way inevitably into the solution and are held by the crystals, appearing in the fused calcium bromide at the end as minute black specks of carbon. When the salt has been filtered just before the last crystallization, such undesirable irregularities are absent. The efficacy of the process of purification was in every case greatly increased by means of the centrifugal drying of the crystals with the help of a centrifuge composed of swinging platinum funnels driven at a high speed by an electric motor. All the operations of transference and evaporation were effected inside of a glass house erected on the laboratory desk, composed of large glass plates held together by a light framework of wood. These plates had been carefully rounded on the edges with a file and protected by split rubber tube, so as to protect the edges and prevent the rubbing off of small particles of glass. An electric stove with a quartz top provided a source of heat for all these operations.

Silver.—The silver was prepared in a manner essentially similar to that used in other recent investigations in Harvard University. It was many times recrystallized as the nitrate, precipitated as pure silver by means of ammonium formate, and fused on boats of pure lime in a stream of pure dry hydrogen. For further particulars previous papers from this laboratory should be consulted.[1]

The Drying and Melting of Calcium Bromide, and the Neutrality of Its Solution.

The salt crystallizes with six molecules of water of crystallization, and dissolves in this water of crystallization at about 38°. As in the case of other concentrated solutions, of similar kinds, the quantitative expulsion of the water from this solution is a difficult matter. Accordingly, in order to dry the salt, the method was adopted which had been used successfully in the earlier analyses of calcium chloride by one of us. The salt was in the first place dried in a desiccator warmed to a temperature just below the "melting point" of the crystallized salt, pure lime being used as the desiccating agent. The water then escapes with considerable rapidity from the crystals, leaving a quantity of effloresced material whose melting point is above 200°. The evaporation of the water from the crystals is of course much hastened by having the vacuum as perfect as possible; accordingly the vacuum desiccator was thoroughly exhausted at a low temperature by means of a Geryk pump. The salt itself was placed in a flat platinum dish. After remaining about eight days in the desiccator, the temperature in the thermostat containing this apparatus could be raised to 50 or 60°, and after eight days more the dehydration had proceeded so far that the water could be all driven off at a much higher temperature without danger of partial melting and the projection of drops of the solution.

In order to eliminate the last traces of water, the salt was melted as usual in a current of hydrogen mixed with hydrobromic acid. This last substance is necessary to prevent the partial decomposition of the salt by the remaining trace of water at a high temperature. The temperature was raised very slowly so that as much water as possible should be driven off from the salt while it was still in a solid condition, and only at the every end was the temperature raised to the melting point at a red heat. The heating was conducted electrically by means of a ribbon of an alloy of nickel and chromium wound directly around the quartz tube which contained the platinum boat holding the calcium bromide to be melted. The progress of the fusion could be watched through the spaces between the ribbon. For twenty minutes the calcium bromide was kept in a fused condition at a medium red heat; and by means of light rapping on the tube the mobile liquid was freed as much as possible from bubbles of gas. When this heating had been finished the hydrogen and hydrobromic acid were shut off, and pure nitrogen was led into the tube, at the same time lowering the temperature to about 400°. After all trace of hydrobromic acid had been driven out, the salt was allowed to cool in a stream of nitrogen, and finally this gas was replaced by pure air. The succession of gases was provided by means of suitably arranged purifiers, all connected by glass stopcocks in a method which has been described in previous communications. The quartz tube was attached to the familiar Harvard "bottling apparatus" by means of which the pure anhydrous bromide was enclosed in a weighing tube in an atmosphere of pure air, and after it had become completely cooled this weighing tube was taken out and placed in a desiccator for at least five hours near the balance by means of which it was to be weighed. Successive weighings of the boat and bottle never differed more than 0.02 milligram. The empty boat and weighing bottle were weighed both before and after the determination. For this purpose they received precisely the same treatment as during an analysis, the boat being ignited in the bottling apparatus, and prepared for weighing just as if it contained calcium bromide. The similarity of treatment affords the best means of avoiding constant errors. That the apparatus served its purpose is clear from the fact that in two cases wherein specimens of melted and weighed bromide were once more melted and weighed, no change exceeding a few hundredths of a milligram was to be observed. The loss of weight of the boat during fusion was never over one-twentieth of a milligram, and sometimes amounted to nothing at all.

---

[1] See especially Richards and Wells, THIS JOURNAL, **27**, 472 (1905). *Pub. Carnegie Inst.*, **28**, 16 (1905). *Z. anorg. Chem.*, **46**, 70 (1905). "Experimentelle Untersuchungen," T. W. Richards [Hamburg, 1909], p. 703.

The bromide was dissolved in water in a large Erlenmeyer flask capable of holding three liters, with a ground stopper. The details were similar to those in the case of lithium chloride,[1] except that the testing for neutrality was somewhat different, because calcium bromide is decidedly a less stable salt than most of the other halides which have been studied in this laboratory, and therefore is less easy to obtain in a state of perfect neutrality. When heated with either air or with water, it is certain to lose some bromine and become alkaline. On the other hand, when heated with hydrobromic acid, a trace of this gas is dissolved. This trace is indeed quickly liberated on further fusion in nitrogen, but if the nitrogen is not absolutely pure, there is danger of overstepping the mark and making the salt slightly alkaline in this process. Therefore every sample of calcium bromide must be carefully tested in order to be sure of its perfect neutrality; and because the salt is slightly hydrolyzed in aqueous solution, the only satisfactory method of testing it is to compare the solution of the fused salt with a solution of the same concentration made from the purest calcium bromide many times recrystallized. The latter, if prepared with adequate care, is presumably neutral, for there is no evidence that either hydrobromic acid or lime tend to go into the crystals to any perceptible extent. In order, therefore, to determine the deviation from neutrality of the fused calcium bromide, it was dissolved in a small amount of water, and to it was added 10 cc. of a saturated aqueous solution of the slightly soluble methyl red, the only indicator which seemed to serve well for this purpose. To the same volume of a solution containing the crystallized salt, assumed to be neutral, was added a like volume of the solution of methyl red, and the colors of the two solutions were compared. When the colors of the two solutions appeared identical, it was reasonable to infer that the fused salt was perfectly neutral. This occurred in two out of the twelve cases. In most cases the fused salt was found to be either slightly alkaline or slightly acid, but two or three drops of the corresponding hundredth normal solution were enough to restore perfect neutralization, except in one case when five drops were required. The appropriate corrections were of course made in the weighings of fused calcium bromide to eliminate the errors which would otherwise have existed in the results because of this lack of neutrality. The absence of such corrections was one of the chief reasons why the ten preliminary results, not worthy of recording here, varied among themselves by amounts distinctly greater than those to be noted in the final results, recorded later.

---

[1] Richards and Willard, THIS JOURNAL, 32, 4 (1910). *Pub. Carnegie Inst. of Washington*, 125.

After the testing for neutrality, the solution was diluted with a liter of the purest water, and the boat was removed by means of a platinum wire, and very thoroughly washed with all possible care. The analysis of the bromide was then carried out by either one of the two usual methods, namely, either the determination of the exact amount of silver equivalent to the calcium present, or the weighing of the precipitated silver bromide. These two processes were never executed in the same experiment in either of the final series, because each can be done more satisfactorily if attention is concentrated upon it alone.

Balance and Weights.—The weighings were made upon a very good balance of Prussian manufacture which had been thoroughly tested and was easily sensitive to 0.01 mg. The gilded brass weights were standardized according to the method usually employed in this laboratory and were often further tested during the progress of the research. As usual, all readings were made by substitution, the substituted tare being an object similar in all respects to that which was being weighed.

It was necessary to determine anew the specific gravity of calcium bromide, because the published values of this constant are highly discrepant among themselves, differing to an extent sufficient to influence appreciably the calculation of the true weight of the substance. This determination was carried out in a pycnometer for hygroscopic solids described by Baxter.[1] Toluene was used as a fluid to be displaced. The sample had been distilled over sodium and was found to have at 25° a density of 0 8605 as the mean of three trials. With this apparatus 2 09625 grams of calcium bromide displaced 0 5378 gram of toluene and 2.974 grams of calcium bromide displaced 0.7629 gram of toluene, the readings being reduced to the vacuum standard. These two determinations give as the specific gravity of calcium bromide the values 3.354 and 3.353, respectively—results essentially identical.

The vacuum corrections to be applied to silver, silver bromide and calcium bromide, when the readings were conducted in air at normal pressure and at 20°, were taken as —0.030 mg., +0.041 mg. and +0 218 mg., respectively, the specific gravity of the brass weights being 8.3. The small changes due to changing pressure and temperature were almost always negligible with these dense substances.

The Determination of the Silver Corresponding to Calcium Bromide.

A weight of purest silver as nearly as possible equivalent to each portion of carefully weighed bromide (as found in the preliminary experiments) was dissolved in nitric acid in a large flask with bulbs to prevent the escape of spray; and the solution was warmed until the nitrous vapors had been wholly driven out. The solution was then diluted so that it contained not more than 10 grams of silver in a liter of water. Every drop of solution was then added in the red light of the dark room to the corresponding bromide solution, little by little, the latter liquid being kept in continual motion. The flask which had contained the silver was of course washed with the greatest care, and the last washings were tested in a nephelometer in order to be sure that every trace of silver had been removed. The mixture had in every case, after precipitation, a volume of about 2.5 liters. It was at first only gently shaken in order to promote complete precipitation without causing the precipitate to cohere into impenetrable balls; and the mixture in this state was left for twenty-four hours in the dark room covered with a black cloth in order that complete equilibrium might establish itself between the precipitate and the solution. In this way opportunity is given for the washing out of any excess of either reagent which may be occluded by the spongy precipitate. When this is accomplished, the mixture is violently shaken for twenty minutes, the flask being closely stoppered. Under this treatment the precipitate coheres satisfactorily and deposits itself after short standing so completely that the small particles which cling to the flask above the level of the liquid can easily be washed down into the flask by tilting the latter backwards and forwards, thus causing the clear liquid to wash every portion of the neck.

---

[1] Baxter and Hines, *Am. Chem. J.*, 31, 220 (1904).

During this whole time the flask was never opened and especial care was taken that no traces of the precipitate should be held in the control space between the lower end of the stopper and the wall of the flask.

The mixture was now ready for filtration. In order to prevent the ejection of drops of liquid on the removal of the stopper, the air in the flask had been slightly warmed by means of the hands before this stopper had been applied in the first place, so that on opening the flask for filtration air was drawn in and not expelled. Cooling the flask with cold water before opening increased this effect. Upon the removal of the stopper, the neck of the flask and stopper were carefully washed with the purest water; and when the solution had been mixed by two or three rotations of the flask, two samples of the clear mother liquor were taken out and placed in two test tubes. To one was added a solution of a milligram of silver; to the other a corresponding amount of potassium bromide; and both were stirred by suitable bent rods. The comparison of the two tubes in the nephelometer enabled one to see at once whether the bromide or the silver was in excess, and it was easy to be sure of an amount corresponding to 0.05 milligram of silver or of bromide in a liter of the solution. If one or the other was found to be deficient, the corresponding amount was added to the whole mass of the solution, and after new shaking and standing another trial in the nephelometer was made. This process was repeated until the nephelometer showed the end point of the reaction, both tubes exhibiting like opalescence. Incidentally it may be noted once more that the liquids in the nephelometer tubes must be allowed to stand for at least 1.5 to 2 hours after they have been precipitated, otherwise the precipitates do not attain constancy. It is essential that during this time, indeed as promptly as possible after they have been filled, the tubes should be covered with glass caps made of rings sealed to round plates of plane optical glass in order to prevent the access of dust and the resulting serious errors in the outcome. The nephelometer can easily detect 1/3000 of a milligram of chlorine, and a single mote of dust may contain this amount.

The following table gives the results of the last six analyses, carried out in this way. It is worthy of note that these analyses are all consecutive ones, the thirteenth not having been brought to a conclusion on account of a mistake in weighing the silver. No finished analysis was rejected:

THE RATIO OF CALCIUM BROMIDE TO SILVER.

No. of exp.	Weight of calcium bromide in vacuum	Weight of silver in vacuum.	Ratio $CaBr_2:2Ag$.	Atomic weight of calcium, Ag = 107.88.
11	4.20860	4.54252	0.926490	40.068
12	4.58644	4.95025	0.926507	40.071
14	5.34866	5.77301	0.926491	40.068
15	7.23724	7.81126	0.926514	40.073
16	4.67673	5.04779	0.926491	40.068
17	7.41636	8.00455	0.926518	40.074
	Sum, 33.47403	36.12938	Average, 0.926502	40.0703

From these six analyses it would appear that the atomic weight of calcium is to be taken as 40.070, if silver is taken as 107.88 (the present international value). The extremes 40.068 and 40.074 deviate but slightly from the mean, and the so-called "probable error" of the average is only 0.0007. The series is as concordant as could reasonably be expected, and except for one possibly insignificant fact would go entirely unchallenged. This fact is the hitherto unexplained circumstance that the experiments where larger quantities of material were used gave slightly higher results than those where smaller quantities were used. The same circumstance is to be noted in the second series of results to be recorded shortly. The agreement of the verdict of these two series may be merely a coincidence, and in any case the deviation is so slight as to cause uncertainty only in the third decimal place of the atomic weight. If, as is probable, the results with the larger quantities are somewhat more accurate, the value 40.07 may be slightly too low; but the true value is not likely to be as high as 40.08.[1]

A more reassuring conclusion may be drawn from another aspect of the results. It is satisfactory that the two different preparations of bromide gave results essentially identical. The specimen recrystallized nine times, which was used in analyses 16 and 17, gave as the mean value 40.071, whereas that which had been recrystallized four times (used in analyses 11 to 15) gave 40.070, a result essentially identical. This seems to indicate that both preparations were really pure; for it is not probable that if impurities had been present a product crystallized nine times would have shown precisely the same result as one crystallized only four times, especially when one considers that the recrystallization was carried out with the help of an energetic centrifuge.

The Determination of the Relation of Calcium Bromide to Silver Bromide.

The method of precipitation of silver bromide for weighing was essentially similar to the method used in previous cases in this laboratory. Only a very slight excess of silver was used in precipitating in order to avoid occlusion of silver nitrate. The precipitation was accomplished in the manner just described and a platinum Gooch-Munroe crucible was used for filtration.[1] The precipitate was first washed seven to ten times by decantation with small quantities of the purest water, and finally was washed upon the filtering crucible by means of a jet driven by hydrostatic pressure. Both mother liquor and wash water were preserved separately and carefully tested in the nephelometer for the traces of bromide which they might contain. The mother liquor rarely contained a trace of bromide, the wash water usually about 0.2 milligram per liter. The filtration was conducted under a glass roof, which served to protect the crucible from dust. The flask in which the precipitation had been conducted was finally washed with a small quantity of the purest freshly distilled, concentrated ammonia, in order to dissolve any trace of silver bromide which might have escaped transference into the crucible. After neutralization with the purest nitric acid this mixture too was tested in the nephelometer with excess of silver solution. In making the nephelometric tests, comparison was made in each case with a standard prepared in precisely the same way.

As usual, the dry precipitate, after having been weighed, was transferred to a small porcelain crucible, weighed again, cautiously heated, and weighed for the third time. The fused mass, which was distributed over the inside surface of the crucible by gently rotating the crucible while inclined at a small angle, was a clear yellow upon cooling and gave evidence of being very pure. The loss during melting was never more than 0.004 per cent. and was usually much less.

These rather complicated processes are subject to somewhat greater possibilities of error than the much simpler comparison with silver, but the agreement of the results was, as a matter of fact, about the same as before. The six analyses recorded in this table represent a series from which none is omitted. They were carried out after the necessary experience gained in preliminary determinations.

THE RATIO OF CALCIUM BROMIDE TO SILVER BROMIDE

No. of exp.	Weight of calcium bromide in vacuum.	Weight of silver bromide in vacuum.	Ratio $CaBr_2 \cdot 2AgBr$	Atomic weight of calcium AgBr = 187.796.
18	10.18591	19.13778	0.532241	40.073
19	7.92400	14.88810	0.532237	40.072
20	6.78048	12.73961	0.532236	40.072
21	6.45970	12.13702	0.532231	40.070
22	5.95390	11.18684	0.532225	40.067
23	5.15998	9.69513	0.532225	40.067
	Sum, 42.46397	79.78448	Average, 0.5322323	40.0702

A glance at this table shows that the figures recorded in it afford a complete confirmation of the results contained in the first table, although these were reached by a different road. Indeed the final averages (40.0702 and 40.0703) are almost precisely the same in the two cases, far within the almost equal "probable errors" (0.0007) of the two series. In the present case, as in the other, the greatest deviation from the mean is about 3 in the third decimal place of the atomic weight of calcium, or about 1 in 70,000 in the total weight of the calcium bromide; this seems to be about the limit of reasonable accuracy in such experimentation. The result, as in the other case, is probably to be regarded as a minimum value, and it seems fairly safe to conclude that the atomic weight of calcium is between 40.07 and 40.08.

---

[1] Richards and Mueller, *Z. anorg. Chem.*, **53**, 438 (1907); THIS JOURNAL, **29**, 651 (1907).

Obviously, because the two series give identical results, the atomic weight of bromine computed from the two average results is equal to that assumed in the calculation of each series, namely, 79.916, if silver is 107.88. This shows that the calcium bromide was free from chloride, and that the occlusion of other salts by the silver bromide must have been imperceptible.

We have already obtained some interesting confirmatory results with calcium chloride, which will soon be ready for publication, and hope to continue the study of this atomic weight and to settle such points as remain obscure.

Summary.

The results of this paper may be stated in a few words, as follows:

Methods for the preparation, dehydration, and melting of pure calcium bromide were devised.

Calcium bromide proved to be less stable on melting than the corresponding barium and strontium salts. By comparison with pure crystallized salt with the help of methyl red, the very slight deviations of the several specimens of melted bromide from exact neutrality were determined in their aqueous solutions.

The density of melted calcium bromide was found to be 3.353 at 25°.

33.47403 grams (in vacuum) of calcium bromide required 36.12938 grams (in vacuum) of silver for complete precipitation. Again, 42.46397 grams (in vacuum) of calcium bromide yielded 79 78448 grams (in vacuum) of silver bromide, each set of figures being the sum of the quantities used in six consecutive determinations. The two ratios give essentially the same value for the atomic weight of calcium, 40 070, if silver is taken as 107 88. The value becomes 40.066 if silver is taken as 107.87. This result is probably a minimum value; but it is improbable that the true one exceeds 40.08.

The investigation shows that the preliminary Harvard work yielded a value for the atomic weight of calcium much more probable than that found by the only other modern investigator.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHTS OF SILVER AND IODINE.

[SECOND PAPER.]

THE RATIO OF SILVER TO IODINE.

BY GREGORY PAUL BAXTER

Received October 22, 1910

Introduction.

In a recent investigation upon the atomic weights of silver and iodine, Baxter and Tilley[1] determined the ratio between silver and iodine pentoxide to be 0 646230. Then, the ratio of silver to iodine having previously been found by Baxter[2] to be 0 849943, the per cent. of iodine in the pentoxide was calculated, and thence the atomic weights of iodine and silver. Since the results obtained in this way were unexpectedly low, 126.891 and 107 850 respectively, while several recent investigations, especially that of Richards and Willard[3] on the ratio of lithium chloride to lithium perchlorate, have shown the atomic weight of silver to be not far from 107 871, and since all known possible causes of error in the determination of the ratio of silver to iodine pentoxide were very carefully investigated, it was possible that the final results might have been influenced by an error in the ratio of silver to iodine. This error need be only very slight to explain the discrepancy, because a given percentage error in the ratio of silver to iodine produces one three times as large in the atomic weights of iodine and silver, but in the opposit direction.

In the determination of the ratio of silver to iodine[4] the preparation of silver iodide in every case formed one step in the procedure. The latter substance is, however, difficult to obtain in a pure condition on account of its strong tendency to occlude soluble silver salts. The difficulty was eliminated as far as was possible at the time, either by precipitation of the silver iodide in ammoniacal solution, or by precipitation at high dilution, these precautions having been shown by both Köthner and Aeuer[5] and Baxter[6] to be beneficial. The evidence obtained in the investigation upon iodine pentoxide indicates that even the pains taken in the early work upon the silver-iodine ratio to avoid occlusion by the silver iodide may not have been sufficient entirely to eliminate the difficulty, and hence that the above value of the silver-iodine ratio is too high. Furthermore, it is noticeable that many of the earlier results upon the silver-iodine ratio indicate a perceptibly lower value for the ratio than the one given above, while most of the possible errors would have tended to produce too high a result. Hence new experiments were instituted for the investigation of the silver-iodine ratio.

---

[1] THIS JOURNAL, **31,** 201 (1909).

[2] *Proc. Am. Acad*, **40,** 419 (1904); **41,** 73 (1905) THIS JOURNAL, **26,** 1577; **27,** 876.

[3] *Pub. Carnegie Inst*, No. 125 (1910). THIS JOURNAL, **32,** 4.

[4] Baxter, *Loc. cit.*

[5] *Ann.,* **337,** 123 (1904).

[6] *Proc. Am. Acad.,* **41,** 77 (1905). THIS JOURNAL, **27,** 880.

It seemed highly desirable in these new experiments to carry out the determination of the ratio of silver to iodine in as nearly as possible the same way as in the determination of the ratio of silver to pentoxide, and also to use material which had been purified in as nearly as possible the same way. Thus constant errors which might enter into the determination of the latter ratio would be likely to be compensated by similar errors in the determination of the former ratio.

The method, in brief, was as follows: Weighed quantities of iodine were reduced to hydriodic acid by a solution of hydrazine hydroxide. After considerable dilution the iodine was precipitated as silver iodide by a very dilute solution of silver nitrate containing a few tenths of a milligram excess of silver. The clear supernatant solution was carefully filtered and evaporated to small bulk, and the excess of silver was determined gravimetrically as silver iodide.

Purification of Materials.

Iodine.—Three specimens of iodine were employed. Sample 1 was made from iodic acid remaining from the research upon iodine pentoxide.[1] The iodic acid had been prepared by the action of the purest fuming nitric acid upon very pure iodine, in quartz vessels, and had been crystallized ten times from aqueous solution in a quartz dish.

A second specimen of iodic acid was made from potassium iodate in the following manner: Potassium permanganate was allowed to react with potassium iodide in concentrated hot solution. The products of this reaction are potassium iodate, potassium hydroxide and manganese dioxide. After the precipitated manganese dioxide had been separated from the solution by decantation and filtration, the solution was evaporated to crystallization, and the crystals were carefully separated from the mother liquor by centrifugal drainage. The mother liquor was several times evaporated until the greater part of the iodate had been recovered. A second portion of potassium iodate was made by allowing potassium permanganate to react in concentrated solution with iodine after the addition of a small quantity of potassium hydroxide. The iodine was probably dissolved by the hydroxide with the formation of iodide and iodate, and the iodide was then converted to iodate by the permanganate. At any rate, the products of the reaction were, as in the previous instance, potassium iodate, potassium hydroxide, and manganese dioxide, the hydroxide being formed in smaller proportions than before. The potassium iodate was obtained from the solution by crystallization as described above. Both portions of iodate were combined and purified by one recrystallization from aqueous solution, with centrifugal drainage.

---

[1] Baxter and Tilley, *Loc. cit.*

From the potassium iodate barium iodate was next prepared by adding to a hot solution of the potassium iodate a hot solution of a nearly equivalent amount of barium hydroxide. The precipitated barium iodate was very carefully washed by decantation with cold water. Very little loss of material takes place during this washing since the barium iodate is only slightly soluble in cold water. The barium iodate, suspended in a comparatively small amount of water, was then converted into barium sulphate and iodic acid by means of an approximately equivalent amount of sulphuric acid at boiling temperature. Since reactions of this sort, which involve the change of one solid into another, progress to completion only with difficulty, the barium sulphate was left in contact with the solution for several days with intermittent heating and shaking. Finally the solution of iodic acid was separated from the barium sulphate by decantation, and was evaporated to small bulk in a platinum dish. Further decantation allowed the removal of traces of barium sulphate which were suspended in the original decantate. The solution was finally evaporated to crystallization in the platinum dish. Somewhat more than a kilogram of iodic acid was prepared in this way.

The final purification of the acid was effected by a long series of crystallizations, as described in the latter part of the paper by Baxter and Tilley.[1] The first mother liquor was found to contain a slight excess of sulphuric acid. This was shown to have been eliminated during the first crystallizations by reducing portions of the mother liquors and testing for sulphate. The barium sulphate, whether dissolved or suspended, was effectually removed during the crystallizations, the solution of acid being occasionally decanted from traces of insoluble material which were present during the first crystallizations. In all, this iodic acid was subjected to eleven crystallizations, the usual process of fractional crystallization being followed in order to avoid too serious loss of material owing to the high solubility of iodic acid, even at ordinary temperatures.

Since chlorides and bromides are not converted to the salts of the oxyhalogen acids by permanganate, it seems probable that the first portion of potassium iodate was free from the corresponding salts of chlorine and bromine. Whether this is true of the second portion, made from iodine, is doubtful, since if the original iodine contained these two elements they would have dissolved in the alkaline solution with the production, to some extent, of chlorate and bromate. Later, however, after the conversion of the iodate to iodic acid, free chloric and possibly bromic acids must have been either vaporized or decomposed during the subsequent treatment.

---

[1] THIS JOURNAL, 31, 216 (1909).

This material differed in its preparation from that used in the earlier determinations of the ratio of silver to iodine pentoxide, and hence a portion of it will soon be used for new determinations of the latter ratio. Iodine made from this iodic acid is designated Sample II.

For comparison with the iodine obtained from the iodine pentoxide, two experiments were made with a third specimen similar to the iodine used in the earlier determinations of the ratio of silver to iodine. This iodine was first distilled from solution in potassium iodide. The product was thus freed from all but traces of chlorine and bromine. Next it was converted into hydriodic acid by suspending the iodine in water and passing hydrogen sulphide through the solution until reduction was complete. The solution of hydriodic acid was boiled to coagulate the sulphur and was filtered. In order to free the hydriodic acid from hydrocyanic acid which might have had its source in iodide of cyanogen contained in the original material, the solution was boiled for several hours until the concentration approached that of the constant-boiling solution. From this hydriodic acid the iodine was set free by the addition of a very nearly equivalent amount of potassium permanganate and distillation into a flask cooled with running water. In this way, since only five-eighths of the iodine is set free by the permanganate, the iodine was a second time distilled from an iodide. The product was distilled once with steam, and after drainage was dried over concentrated sulphuric acid. This specimen is designated Sample III.

Silver.—Several samples of silver were used, most of which have been employed in other similar investigations. Sample A was purified by Mr. A. C. Boylston for work upon the analysis of phosphorus tribromide.[1] This material was prepared by first precipitating the silver as chloride from strongly acid solution, with subsequent reduction by means of sodium hydroxide and sugar. The metal was fused upon charcoal before a blowpipe and the surface impurities were removed from the buttons by scrubbing with sea sand and etching with dilute nitric acid. The cleansed buttons were dissolved in nitric acid, and the solution, after neutralization, was precipitated with ammonium formate which had been prepared with distilled materials. The metal was thoroughly washed with water and was again fused with even more care than before in a crucible lined with the purest lime. The resulting buttons were in turn cleansed by etching with dilute nitric acid and were next converted into electrolytic crystals in a cell in which a concentrated, nearly neutral solution of silver nitrate served as electrolyte, and a pile of the buttons served as anode, the cathode being a stick of very pure silver from another preparation. After the crystals had been very thoroughly washed with water, they were fused in a current of hydrogen in a porcelain boat lined with the purest lime. The boat was provided with cavities so that the buttons of silver varied considerably in size, from 2 to 5 grams. The final product was cleansed from adhering lime by etching with dilute nitric acid and, after being washed with the purest water, it was dried, first in air at 100°, finally in a vacuum at about 500°.

---

[1] Not yet published.

Sample B was prepared in an exactly similar fashion by Dr. H. C. Chapin for work upon the atomic weight of neodymium,[1] except that it was necessary to cut the product into smaller fragments by means of a jeweler's saw. Surface contamination with iron from the saw was removed by etching with successive portions of dilute nitric acid until the acid remained free from iron. Sample C was purified by Mr. Victor Cobb for work upon the analysis of ferrous bromide in a way exactly similar to that used in the purification of Sample A.[2] Sample D was used in an investigation upon the atomic weight of bromine.[3] This material had been precipitated once as silver chloride. The product was reduced with sodium hydroxide and sugar and was twice deposited electrolytically as described above in the case of Sample A.

These methods of purification have already been discussed and shown to be efficient in several papers from this laboratory, especially by Richards and Wells.[4] As will be seen later, the different specimens of silver all gave essentially identical results in this investigation. Several of them have already been compared, with a like outcome.

The Ratio of Silver to Iodine.

In the earlier determination of the ratio of silver to iodine the method employed was as follows: Iodine was sublimed into a weighed tube; next, after being weighed, it was reduced by means of sulphurous acid, and the very dilute solution of iodide was precipitated with a very dilute solution of an equivalent amount of silver nitrate. The end point was then determined in a nephelometer.

In the present instance certain very considerable modifications of the earlier method were made. In the first place, owing to occlusion of silver sulphate by silver iodide, sulphurous acid has been found to be unsuitable as a reducing agent,[5] hence hydrazine hydroxide was substituted. The products of reduction were, therefore, only nitrogen gas and hydriodic acid. In the second place, in the investigation upon the ratio of silver to iodine pentoxide it was found that, even if exactly equivalent amounts of silver and iodine are employed, the end point as determined in a nephelometer is somewhat uncertain, owing to the great dilution of the mother liquor and, in all probability, to disturbances due to traces of colloidal precipitate.[1] Therefore, as in the investigation upon iodine pentoxide, instead of attempting to determin the end point in this way, a very slight excess of silver was used, and the excess was found by evaporating the mother liquor to very small bulk and then estimating the silver gravimetrically as silver iodide. Owing to the strong tendency of silver iodide permanently to occlude silver nitrate, the excess of silver was very small indeed, as a rule less than 0.2 milligram. Furthermore, both the solution of the iodide and the solution of silver nitrate were made very dilute before precipitation in order to avoid as far as possible the aforesaid occlusion. In the third place, much larger quantities of material were employed so that accidental errors should be of less significance.

---

[1] *Proc. Am. Acad.*, **46,** 213 (1910).

[2] This investigation will soon be published.

[3] Baxter, *Proc. Am. Acad.*, **42,** 201 (1906); THIS JOURNAL, **28,** 1322.

[4] *Pub. Carnegie Inst.*, No. **28,** 16 (1905). THIS JOURNAL, **27,** 472.

[5] Baxter and Tilley, THIS JOURNAL, **31,** 208 (1909).

In all but the last three experiments the tube in which the iodine was weighed was of glass, about 18 centimeters long and 1.8 centimeters in external diameter. The ends of the tube were constricted and were provided with well fitting ground-glass caps in order to avoid vaporization of the iodine during the weighing of the tube and the subsequent manipulation.

The iodine was prepared for weighing by first dehydrating a suitable quantity of iodic acid in a platinum boat in a current of pure dry air, as described in the paper upon the analysis of iodine pentoxide. The air was purified by being passed over hot copper gauze, and then through a system of towers containing in succession glass beads moistened with silver nitrate solution, a solution of potassium hydroxide containing potassium permanganate, and concentrated sulphuric acid containing a small amount of potassium dichromate. The final drying of the air was effected with phosphorus pentoxide which had been freshly sublimed in a current of oxygen. The apparatus was constructed wholly of glass with fused joints. The boat containing the iodic acid was placed in a hard glass tube through which the current of air was passed, the tube being heated by means of the solid aluminium oven which has been described elsewhere.[2] The first stage of the dehydration of iodic acid takes place rapidly at 100° if it has been previously ground with a small percentage of the substance produced in the first stage of the dehydration, $HIO_3.I_2O_5$. Inoculation with this phase not only reduces the temperature at which the dehydration begins, but also diminishes the proportion of moisture finally retained by the pentoxide.[3] As soon as water ceased to be given off, the temperature was raised until the second and final stage in the dehydration began, at about 220°. Finally the pentoxide was

[1] Baxter and Tilley, THIS JOURNAL, 31, 210 (1909).

[2] Baxter and Coffin, *Proc. Am. Acad.*, 44, 184 (1909). THIS JOURNAL, 31, 206.

[3] Baxter and Tilley, THIS JOURNAL, 31, 212 (1909).

heated for one hour at 240°. Iodine pentoxide which has been dried in this way has been found to contain only a little over 0.002 per cent. of residual moisture.[1] The water formed during the dehydration was, of course, carefully expelled by heating the hard glass tube.

Next the iodine pentoxide was converted into iodine and oxygen by heating the section of the tube containing the boat to about 350°. The iodine was allowed to condense in the cooler portions of the tube beyond the boat, although, of course, a slight loss of iodine took place. During this decomposition it seems certain that the trace of residual moisture in the pentoxide must have been eliminated. Nevertheless, for the sake of certainty, before the iodine was sublimed into the weighing tube, it was heated slightly above its melting point, 114°, in the current of dry air. The weighing tube was then placed in position, with the constricted end of the hard glass tube inserted for a short distance into one end of the weighing tube, the weighing tube being supported upon a glass stand. The iodine was slowly sublimed into the weighing tube by gently warming the hard glass tube. Finally the iodine in the weighing tube was heated to fusion and allowed to solidify. The caps were placed on the weighing tube, which was allowed to stand near the balance case, under a bell jar containing concentrated sulphuric acid, for several hours. During the manipulation the weighing tube was handled only with clean, cork-tipped forceps.

Since during the sublimation of the iodine the hard glass tube must have been slightly attacked, and since it is possible that alkali iodides thus formed could have been carried into the weighing tube with the iodine, a quartz tube was substituted for the hard glass tube after the first five experiments. This tube was provided with several constrictions beyond the section in which the boat was placed, which served the purpose first of preventing to a considerable extent the conduction of heat along the tube, and second, of preventing back diffusion of iodine. Since a small amount of undecomposed pentoxide was carried along by the rather rapid current of oxygen evolved during the decomposition, the first constriction in the quartz tube was loosely filled with a roll of platinum gauze which was heated to redness, so that any pentoxide which reached this constriction must have been completely converted to iodine and oxygen. As a matter of fact, neither of these changes produced any perceptible effect upon the results.

When iodine from Sample III was employed, it was sublimed from a platinum boat into the quartz tube and once again from one portion of the tube to another before the final sublimation into the weighing tube.

In order to reduce the iodine to hydriodic acid, it was next dissolved in a solution of an excess of hydrazine hydroxide. A thick-walled flask of Jena glass holding nearly two liters was provided with a column of bulbs carefully ground into the neck. In the flask was placed a quantity of a solution of hydrazine hydroxide considerably more than sufficient to combine with the iodine. The hydrazine was made from the sulphate by distillation in a platinum still with an excess of sodium hydroxide, and was redistilled before use. The weighing tube containing the iodine was carefully introduced into the flask, the stoppers being removed in the process, and the column of bulbs was put in place immediately after the introduction of the iodine tube. In this manipulation a small quantity of iodine vapor may have escaped from the tube during the very short time in which it was exposed to the air. However, since the total amount of iodine vapor contained by the tube at 20° was not greater than 0 03 milligram,[1] and since certainly only a small fraction of the total vapor could have escaped into the air outside the flask, and especially since the interior of the flask and the column of bulbs had been moistened with hydrazine solution shortly before the iodine tube was introduced so that any iodine vapor in the flask must have been quickly absorbed, the error from this source must have been very small. The solution of the iodine in hydrazine progresses too rapidly if the iodine has not been previously fused, for crystals of iodine, on account of their large surface, reduce so rapidly that the current of nitrogen issuing from the flask might possibly carry with it traces of iodine vapor. Since acid is produced in this reaction, it was found advantageous to keep the solution nearly neutral by the occasional addition of redistilled ammonia. This had two advantages: first it accelerates the rather slow solution of the fused iodine; secondly, it prevents the possible escape of hydriodic acid vapor from the flask. Several tests in which the nitrogen evolved in the reduction was caused to pass from the top of the column of bulbs through a trap sealed with water showed that in fact no iodine was lost in this way.

---

[1] Baxter and Tilley, THIS JOURNAL, 31, 212 (1909).

After the dilution of the iodide solution to a volume of about one and one-half liters, it was transferred for precipitation to an 8-liter bottle with a carefully ground stopper. Whether or not the solution was ammoniacal at this point, about 25 cc. of constant boiling nitric acid were introduced, after the acid had been diluted to a volume of one liter and boiled to destroy nitrous acid; for unless the nitric acid is free from nitrous acid, iodine is set free. The bottle was immediately stoppered after the addition of the nitric acid, and was allowed to stand for some time after any liberated iodine had been reduced by the excess of hydrazine. In all but the earlier experiments the acid was introduced through a long thistle tube at the bottom of the bottle, so that iodine could not reach the surface of the solution until after the bottle was closed. The amount of iodine set free in this way was, however, in no case large enough to have caused appreciable loss by evaporation. If the solution did not at this point have a total volume of nearly four liters, it was next diluted to this volume.

---

[1] The vapor pressure of iodine at 20° is 0.2 mm. Baxter, Hickey and Holmes, THIS JOURNAL, 29, 127 (1907). The interior volume of the tube was less than ten cubic centimeters.

A quantity of silver, a very few tenths of a milligram, in excess of the amount necessary to combine with the iodine, was weighed out, the greater part being in buttons weighing several grams each, the final adjustment of the weight being made with tiny ignited electrolytic crystals. This silver was dissolved in redistilled nitric acid which had been diluted with an equal volume of water, in a flask provided with a column of bulbs to catch possible spatterings. The silver was dissolved so slowly, however, that very little effervescence took place, nitrous acid rather than nitric oxide being formed. The solution was then further diluted and heated until free from nitrous acid. Next the silver nitrate solution was diluted to a total volume of nearly four liters and then was slowly added to the solution of hydriodic acid in the precipitating bottle, with continual agitation during the precipitation. The precipitating bottle was shaken violently for a short time, and was allowed to stand for at least one week with occasional shaking until the supernatant liquid seemed to be absolutely clear. The clear liquid was then filtered through a Gooch-Munroe-Neubauer crucible with a very dense mat of platinum sponge, so that, although the filtration proceeded slowly, there seemed to be certainty that every particle of suspended silver iodide was removed during the filtration. The filtered solution was evaporated to a very small bulk, until the greater part of the free nitric acid had been expelled. Toward the end of the evaporation small quantities of silicic acid separated out. Consequently, before the precipitation of the silver in the evaporated filtrate, it was filtered a second time through the Neubauer crucible. The total volume of the solution, after the second filtration, was not more than 100 cc. and frequently was as small as 50 cc. To this solution was added a quantity of a solution of pure hydriodic acid large enough completely to precipitate the silver. Several days' standing were usually necessary to insure sufficient coagulation of the opalescent silver iodide for filtration. Then the precipitate was collected upon a small weighed Neubauer crucible, and, after being heated to about 200°, it was weighed. In order to show that no silver iodide was lost in this filtration, in several instances the filtrate was evaporated to small bulk and tested nephelometrically for silver, always with essentially negative results. The quantity of silver used in each experiment was so carefully adjusted before precipitation that the silver content of the filtrate seldom amounted to more than 0.5 milligram, and in all but two of the later experiments it was less than 0.2 milligram.

During every experiment the glass tube in which the iodine was weighed lost slightly in weight. In a few cases the loss amounted to as much as 0.3 milligram, although in many it was hardly more than 0.1 milligram. This loss in weight was probably due in part to the action of the iodine on the glass with the formation of soluble iodides. Since these iodides would have dissolved during the reduction of the iodine, the error from this source must have been considerably less than the loss in weight of the tube. Furthermore, it is very probable that the loss in weight of the weighing tube was caused in part by the solvent action of the ammoniacal hydrazine solution and possibly to mechanical abrasion of the ground surfaces during the manipulation.

In the last three experiments the glass weighing tube was replaced by a similar quartz tube with glass caps. Although the loss in weight was somewhat diminished by this change, it was not wholly prevented, the losses in the first two of the three experiments being 0.00010 and 0.00020 gram, respectively. In these three experiments it is more probable that the difficulty was due to the solvent action of the hydrazine solution and to abrasion than to action of the iodine on the quartz. If this is the case, the results would not be at all affected by the loss in weight of the tube.

One of the chief dangers in these experiments lies in the occlusion of silver nitrate by the silver iodide. For this reason the solutions were made as dilute as possible before precipitation. In the first ten analyses the volumes of the two solutions before precipitation were nearly four liters, while in the last three analyses the volumes were between seven and eight liters. Hence the concentrations varied between eightieth normal in analysis 5 and thirtieth normal in analysis 2. The fact that the results seem to be independent of the concentrations is strong evidence that the occlusion could not have been very serious. The attempt was made, however, to secure further evidence that this occlusion was negligible by conducting the precipitation in two analyses (9 and 10) in reverse fashion, *i. e.*, by pouring the hydriodic acid solution into the silver nitrate solution. Although the opportunity for occlusion of silver nitrate was evidently very much greater in these two experiments than in the others, the results of analyses 9 and 10 agree so well with those of the others that very little doubt can exist that the occlusion of silver nitrate had been prevented. Similar evidence was obtained in the analysis of iodine pentoxide.[1]

The solubility of silver iodide has been found by Kohlrausch[2] to be only

[1] THIS JOURNAL, 31, 218.

[2] *Z. physik. Chem.*, 50, 355 (1904).

0.0000035 gram per liter at 21°. In 8 liters of mother liquor there would be dissolved then only 0.00003 gram of silver iodide while the wash waters would contain a trace more. The correction for the equivalent amount of silver or iodine would not amount to more than 0.0002 per cent. in any one of the first ten analyses. In the last three analyses the volume of the mother liquor was at least 16 liters. Hence the dissolved silver iodide amounted to 0 00006 gram. However, since larger quantities of material were used in the last three experiments, the percentage correction due to solubility is no greater.

Evidence that the Neubauer crucible was an effective filtering medium is to be found in the fact that in many of the analyses the quantity of silver iodide obtained from the filtrate was not much greater than the amount which should have been dissolved. Furthermore, in one analysis, the only one completed which is not recorded in the following table, the filtrate was found to contain only a mere trace of silver. The crucible which was employed in all the analyses, with a water pump vacuum, allowed from one to two liters of solution to pass per hour.

In the following table are given the results of all the analyses which were completed, with the exception of the one mentioned above in which no silver was found in the filtrate The silver used in this experiment, if it was exactly equivalent to the iodine, yielded a ratio of silver to iodine very close to the other analyses, 0 849016, but on account of the uncertainty as to whether the silver was sufficient to combine with the iodine, and because the analysis met with a slight accident, it has been considered wiser to omit this result in computing the average.

The weights of the silver and the iodine are corrected to the vacuum standard by subtracting 0.000031 gram for each apparent gram of silver and adding 0 000099 for each apparent gram of iodine.[1] The weights were carefully standardized by the method described by Richards.[2]

Results and Discussion.

A careful examination of the following table shows that neither the variations in the specimens of silver and iodine employed, nor those in the methods of analysis produced appreciable effects upon the results. The extreme difference in the ratio of silver to iodine is 0 007 per cent.; but all except three of the results agree within 0.003 per cent. and the last ten analyses within 0.005 per cent. The final average is 0.005 per cent. lower than the result previously obtained, 0.849943, while no one of the thirteen analyses yielded a result as high as the above figure. This outcome confirms the suspicion previously expressed on page 1591 that the silver iodide obtained in the earlier determinations of the silver-iodine ratio was contaminated by occluded impurities.

---

[1] Calculated from the following specific gravities: Weights, 8.3; silver, 10 49; iodine, 4.93; air, 0.0012.

[2] THIS JOURNAL, 22, 144 (1900).

THE RATIO OF SILVER TO IODINE.

No. of analysis.	Sample of silver.	Sample of iodine.	Weight of silver. in vacuum. Grams.	Weight of iodine in vacuum. Grams.	Weight of silver iodide corrected for solubility. Gram.	Corrected weight of silver in vacuum. Grams.	Ratio Ag : I.
1	A	I	7.65478	9.00628	0.00022	7 65468	0 849927
2	A	I	11 43208	13 45067	0 00062	11 43179	0 849905
3	A	I	10 08602	11.86648	0.00067	10.08571	0 849933
4	A	II	7 24530	8.52461	0.00070	7 24498	0 849890
5	A	II	5 46366	6 42840	0.00033	5 46351	0 849902
6	B	II	7.05651	8.30266	0.00022	7 05641	0 849897
7	B	III	8 45918	9 95288	0 00030	8 45904	0.849909
8	A	II	5 92510	6.97131	0 00042	5 92591	0.849899
9	A	II	7 97952	9 38852	0.00055	7 97927	0 849897
10	C	II	5.58238	6.56811	0 00015	5 58231	0 849911
11	A	III	16 03919	18 87136	0.00036	16.03902	0.849913
12	A	II	15 16312	17.84091	0 00136	15 16249	0 849872
13	D	II	12 71182	14 95666	0 00027	12.71170	0.849902
						Average,	0 849906

When the average ratio is combined with that of silver to iodine pentoxide, 0.646230, the atomic weights of silver and iodine are found to be 107 864 and 126 913, respectively. On the basis of 107 864 for the atomic weight of silver, the older value of the silver-iodine ratio yields 126.907 as the atomic weight of iodine, *i. e.*, the newer value raises the apparent atomic weight of iodine referred to silver by 0.006 unit. It is of interest to note that a positive error of 0.0003 per cent. in the ratio of silver to iodine is necessary to lower the apparent atomic weight of silver by one one-thousandth of a unit, while a negative error of 0.0002 per cent. in the ratio of silver to iodine pentoxide produces the same effect. The agreement of the final value for the atomic weight of silver with that recently found by Richards and Willard, 107.871, is as satisfactory as could be expected from consideration of the widely different methods employed in the two researches. There seems to be little doubt that the atomic weight of silver lies nearer 107.87 than 107.88, the commonly accepted value. Further evidence upon the ratio of silver to iodine is desirable, and it is intended to pursue the investigation by new determinations of the ratio of silver to silver iodide and of silver chloride to silver iodide.

I am very greatly indebted to both the Carnegie Institution of Washington and the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum and quartz apparatus.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.[1]]

THE ATOMIC WEIGHT OF VANADIUM.

BY D. J. MCADAM, JR.

Received October 21, 1910.

Introductory.—In this laboratory, use has frequently been made of dry hydrochloric acid gas in making various separations, and in several atomic weight determinations.

Smith and Hibbs[2] found that vanadium, as well as a number of other substances, could be completely volatilized from their alkali salts by heating in a current of dry hydrochloric acid gas. It therefore seemed probable that this method might be used in determining the atomic weight of vanadium. A new determination of the atomic weight of this element would be particularly desirable since the results obtained by previous investigators differ widely.

Historical.—Berzelius, in 1831,[3] made four determinations of the atomic weight of vanadium. In three of these he reduced V_2O_5 to V_2O_3 by heating in a stream of hydrogen; in the fourth, he reoxidized the V_2O_3 to V_2O_5. As the average of four fairly concordant results, he obtained a value which corresponds to 52 46, referred to oxygen as 16. As Roscoe pointed out later, Berzelius' material undoubtedly contained phosphorus, a small trace of which interferes greatly with the reduction of V_2O_5 to V_2O_3. The ammonium molybdate test for phosphoric acid was unknown in Berzelius' time.

Roscoe, in 1867,[4] made four determinations by the method of Berzelius, using material carefully purified in several different ways. The average of the four results was 51 371, but the maximum and minimum differed by nearly one-half of one per cent.

He also obtained a series of nine values by determining the amount of silver required to precipitate the chlorine from vanadium oxychloride, $VOCl_3$. He did not use the proper end point for this reaction, but the final results would not be affected very much by this error. Loss of chlorine on treatment of the $VOCl_3$ with water was probably a more serious source of error.

In still another series of eight experiments, Roscoe weighed the silver chloride obtained from a known weight of vanadium oxychloride. He does not mention any correction for the solubility of the silver chloride in the wash water; if this was neglected, his value for the percentage of chlorine is too low, and consequently his value for the atomic weight is too high. The variation in the percentage of chlorine in these seventeen experiments is from 60.86 to 61 55, or about 1.13 per cent. This, of course, means a variation in the calculated molecular weight of $VOCl_3$ of 1.13 per cent.; and, since the atomic weights of oxygen and chlorine are assumed to be known, all this variation would apply to the vanadium alone, and would amount to about 3.4 times 1.13, or 3.84 per cent. For example, the maximum calculated value for the atomic weight would be 52.39, and the minimum 50.44. The average of his results by both methods is 51 24.

---

[1] From the author's doctoral thesis.

[2] THIS JOURNAL, 16, 578; *Z. anorg. Chem.*, 7, 41.

[3] *Kgl. Vet. Acad. Handl.*, 1–65 (o); *Ann. Physik*, 22, 1–67.

[4] *Phil. Trans., R. S.* 158, 1–27 (o).

For over forty years our knowledge of the atomic weight of this element rested entirely on the work of Roscoe. Within the last year, however, two articles on the atomic weight of vanadium by Wilhelm Prandtl and Benno Bleyer have appeared.[1] These authors have used the same methods that were used by Roscoe, but have used great care in avoiding the sources of error in the work of the earlier author.

The vanadium oxychloride was carefully purified and kept out of contact with air until it had been weighed. Moreover, on treatment of the oxychloride with water, they reduced the vanadium to the valence of four by means of pure zinc, and thus avoided loss of chlorine.

In order to make allowance for the solubility of silver chloride in water, they prepared twelve wash waters by washing the silver chloride precipitated in the first experiment in each series; the twelve filtrates, in the same order, were used to wash the silver chloride in the remaining experiments of the series.

In the first article published by Prandtl and Bleyer are given the results of two series of experiments by this method. In Series I, consisting of five determinations (the first one being of course rejected), the average percentage of chlorine obtained from the oxychloride was 61.3095 ± 0.0158; the maximum was 61.352 and the minimum 61.284, a variation of 0.11 per cent. This variation, when applied to the vanadium content would be multiplied by 3 4, making 0.37 per cent. variation in the calculated value for the atomic weight. The average value for the atomic weight in this series is given as 51.133 ± 0.013. The authors, however, have overlooked the fact that the probable error in the percentage of chlorine must be multiplied by 3.4 to give the probable error in the atomic weight of vanadium; so it should be ±0.044 instead of ±0.013.

In Series II, consisting of six determinations, the average percentage of chlorine was 61.3696 ± 0.0098, the extremes being 61.405 and 61.348, a variation of 0.093 per cent. This would correspond to a variation of 0.316 per cent. in the atomic weight. The average value for the atomic weight in this series is 50.963, and the probable error as before should be multiplied by 3.4, giving ±0.027 instead of 0.008. As a mean of the two series, they get 51.048 ± 0.010, but it should be 51.048 ± 0.034.

In the second article by the same authors, they have a third series of four accepted values, varying from 61.301 to 61.333 for percentage of chlorine. As an average for the thirteen accepted values of all three series, they obtain 51.061.

---

[1] *Z. anorg. Chem.*, 65, 152; and 67, 257.

In the same article are recorded the results of four determinations by the method of Berzelius. In this series they obtained results that are considerably higher, giving an average of 51.374 ± 0.033; but they found that the V_2O_3 takes up oxygen so rapidly that the weight of the compound cannot be obtained with any certainty. It is therefore probable that the observed weights of V_2O_3 are too great, and consequently the calculated values for the atomic weight are too high.

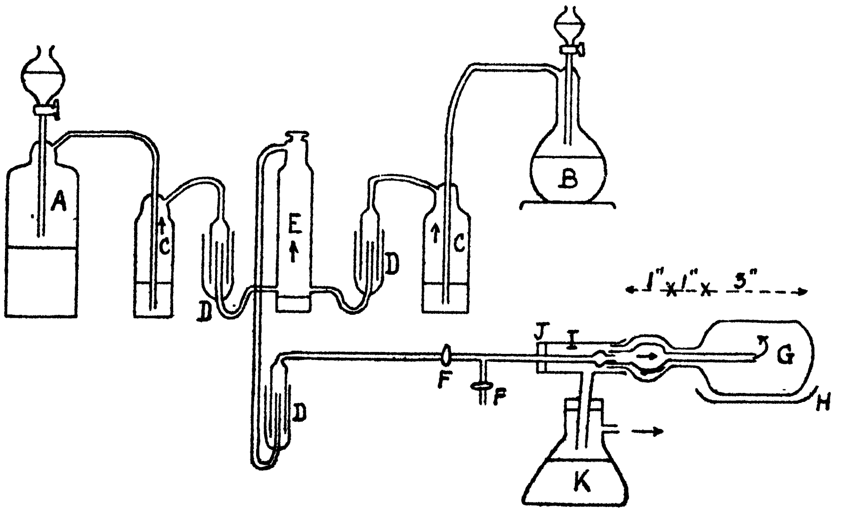
The discrepancies in the results of this careful investigation have thus made more evident the need for a redetermination for the atomic weight of vanadium by a new method.

Method and Apparatus.

The salt of vanadium used in these experiments was sodium metavanadate ($NaVO_3$), the most stable of the vanadates of sodium. Some attempts were made to use other vanadates of sodium, but they were found to be unstable or indefinit.

The metavanadate was heated in hydrochloric acid gas in order to drive out the vanadium and leave sodium chloride. Since the hydrochloric acid has a tendency to reduce vanadates, it seemed probable that a mixture of hydrochloric acid gas and chlorine would drive out the vanadium more readily than the hydrochloric acid alone. Experiments proved that the presence of a small proportion of chlorine had a good effect.

The gas generators and drying apparatus were constructed entirely



of glass, with connections of ground glass or sealed by sulphuric acid; the vessel in which the sodium vanadate was heated was of quartz.

The arrangement of the apparatus is shown in the figure.

In the vessel A, the hydrochloric acid gas is generated by allowing concentrated sulphuric acid to drop into strong hydrochloric acid solution. In B, the chlorine is generated by allowing hydrochloric acid to drop into the flask containing pure potassium permanganate moistened with water. C, C, are drying vessels containing sulphuric acid. D, D, D, are connectors in which sulphuric acid is placed so as to make the connection air-tight. E is a drying tower, containing glass beads moistened with sulphuric acid. F, F are stopcocks so arranged that the gas from the generators can be shut off and a current of pure air substituted. G is the flask containing the sodium vanadate; it is supported by the quartz dish H. I is a tube of hard glass. J is a rubber stopper through which the tube from the gas generator passes. K is a flask containing water, through which the acid fumes from the generator are drawn by suction.

Preparation of Pure Material.

Water.—The distilled water of the laboratory was redistilled once from alkaline permanganate, rejecting the first fourth of the distillate. It was then redistilled twice more, the last time with a block tin condenser; in some of the later preparations a quartz condenser was used. The water seal invented by T. W. Richards was used in all distillations.

When used for crystallizations, the water was either allowed to run from the condenser directly into the platinum dish, or was collected in a quartz flask.

Sodium Metavanadate.—The chief source was iron vanadate that is used in the preparation of ferro-vanadium. It contained not more than a trace of phosphorus or molybdenum.

The iron vanadate was changed to sodium vanadate by boiling with caustic soda or sodium carbonate, filtering off the ferric hydroxide, and evaporating the filtrate to crystallization. It was purified by several different methods, and its freedom from phosphorus and molybdenum was tested and proved.

Sample A.—A mixture of vanadic acid and acid vanadate of sodium was boiled with a slight excess of C. P. sodium carbonate. It was then recrystallized five times in glass from ordinary distilled water, and twice in platinum from twice distilled water. The crystallization was carried on in a room free from acid fumes, so in this sample no special precautions were taken to keep the material out of contact with the air of the room. The sample was dried and preserved in porcelain dishes in a desiccator, over sulphuric acid, that had been boiled with ammonium sulphate.

Sample B.—Some metavanadate containing phosphate, was recrystallized a few times, rejecting the first crop of crystals each time. The phosphate was thus almost completely removed. The partially purified metavanadate was now recrystallized six times in glass and once in platinum from twice distilled water, being drained by suction each time.

It was next crystallized six times more in platinum by dissolving in hot water, cooling, and distilling into the dish some twice distilled alcohol. The substance separated out in small crystals and settled rapidly, leaving a large volume of liquid, which was poured off. It was next recrystallized twice from water, by allowing the crystals to form slowly without stirring. For each crystallization several weeks were required, and considerable liquid was left, which was poured off. The substance was dried and kept in a desiccator over caustic soda.

Sample C.--Some sodium vanadate, which had been crystallized several times, was recrystallized twice more in porcelain, from ordinary distilled water. It was then recrystallized in platinum, three times from ordinary distilled water and three times from thrice distilled water. It was kept in a desiccator over caustic soda during crystallization.

Centrifugal drainage was used during the last five crystallizations, the material being rotated in a perforated platinum cone. Not enough time was allowed to each crystallization, consequently the crystals formed in a pasty mass, which did not drain well. This error was avoided in later preparations.

The crystals were now dissolved in hot water and allowed to stand in a desiccator over caustic soda; crystals formed slowly and the remaining liquid was poured off. The solution was yellow at first, but as crystallization proceeded it became colorless.

Sample D.—The mother liquor from sample C was put in a desiccator over caustic soda and allowed to evaporate to dryness. A little over two grams were obtained, and this was used later as a test for the neutrality of sample C.

Sample E.—Since later results indicated that sample C still contained excess of alkali, a portion of it was recrystallized twice more, with centrifugal drainage, and was washed each time with a little distilled water. The crystallization was allowed to take place slowly; so the substance was not pasty as in sample C, and drained readily, giving a light yellow filtrate. Contact with the air of the room was prevented as much as possible by keeping it in a desiccator over caustic soda during crystallization.

The material had now been put through eleven crystallizations altogether, and later results indicated that it was free from excess of alkali.

Sample F.—Crude sodium vanadate was acidified with sulphuric acid and the precipitated vanadic acid washed repeatedly with distilled water; it still gave a test for sulphuric acid.

It was then treated with a large quantity of water and reduced to vanadyl oxalate by heating with oxalic acid. A slight excess of ammonium oxalate was added and the double ammonium oxalate crystallized out on evaporation and cooling. After three crystallizations, with drainage by suction, no trace of sulphate could be detected, and the material was probably free from phosphoric and molybdic acids.

By addition of excess of ammonia, a brown precipitate of ammonium vanadite was obtained, which was filtered and washed several times. It was then heated to get rid of ammonia, and fused with sodium carbonate. The water solution was still greenish, so the oxidation was completed by addition of a little sodium peroxide. The analyses of the sodium carbonate and sodium peroxide, according to J. T. Baker, showed th following:

	Na_2CO_3 Per cent.		Na_2O_2. Per cent.
Fe	0.0005	Fe	0.003
Al_2O_3	0.0002	Al_2O_3	0.001
CaO	0.008	Cl	0.007
SiO_2	0.001	SO_3	0.001
A	0.085	Na_2O_2	83.1
SO_3	0.001	CO_2	0.32
H_2O	0.95		

The sodium vanadate was now crystallized eight times in porcelain and three times in platinum from ordinary distilled water, suction being used after each crystallization. It was now practically neutral to phenolphthalein. It was next crystallized four times more from thrice distilled water, each time with centrifugal drainage and washing. The last three times the distilled water came in contact with nothing but quartz and platinum.

Special precautions were taken to avoid contact with carbon dioxide of the air during the last few crystallizations.

The effect of carbon dioxide of the air could be only slight, but experiments showed that it affects the equilibrium to a certain extent. To show the effect of carbon dioxide, the gas was prepared by the action of dilute sulphuric acid on sodium bicarbonate, and passed through two bottles of sodium bicarbonate solution, and thence through a vessel containing glass beads moistened with water. The purified gas was then passed into some of the nearly colorless solution of metavanadate, and soon turned the solution deep orange-red. The equation might be epresented as follows:

$$4NaVO_3 + H_2O + 2CO_2 = Na_2V_4O_{11} + 2NaHCO_3.$$

On boiling this orange-colored solution, or putting it in a desiccator over caustic soda, the reverse reaction takes place, carbon dioxide is given off, and the solution becomes colorless. If the metavanadate contains excess of alkali or sodium carbonate, only a faint yellow color appears on passing in carbon dioxide, since the increased mass of bicarbonate favors the reverse reaction.

Metavanadate solutions are usually colorless when hot, and yellow when cold, but an experiment tried on some of the pure material seems to indicate that the yellow color is due to traces of acid vanadate caused by carbon dioxide of the air. A solution of the metavanadate, which was light yellow in color, was heated to boiling in a glass flask. On cooling in contact with the air, a yellow color appeared; but if the flask was stoppered while the liquid was boiling, no color appeared on cooling.

These experiments prove that carbon dioxide of the air can have no effect on the solutions when they are hot; and therefore its effect would be negligible in preparing sodium metavanadate, if the material is kept in a desiccator over caustic soda. The substance which had thus been put through fifteen crystallizations was cream colored. It was neutral in hot or cold solution to methyl orange, litmus or phenolphthalein. The fused substance was colorless and transparent.

Hydrochloric and Sulphuric Acids.—For all but the last two experiments, ordinary C. P. acids were used. Since the method of generating the hydrochloric acid gas was a purification in itself, it was thought that the ordinary acids would be sufficiently pure.

If the hydrochlroic acid contained any hydrobromic acid, the bromine would be set free and driven out by the action of the chlorine. No arsenic would remain with the sodium chloride in the final weighing, since it is easily volatilized by heating in contact with hydrochloric acid gas. Any sulphur dioxide in the sulphuric acid would be oxidized by chlorine and remain in the drying vessels.

Nevertheless, in the last two experiments, special hydrochloric and sulphuric acids were used, containing no arsenic, nitric acid, or sulphurous acid, and only a trace of iron, according to the analysis of J. T. Baker.

Balance and Weights.—A Staudinger balance, sensitive to 0.00001 gram, was used in these experiments. It was kept in the basement, in a room that was used for no other work; the balance rested on a brick and stone support that was sunk directly into the ground.

The weights were kindly loaned by Professor Franklin of the Physics Department of Lehigh University. The larger weights were of brass, gold-plated, and the smaller weights were of platinum. They were carefully standardized, and allowance was made for the buoyancy of the air; the standardization was repeated several times in the course of the experiments.

All weighings were by substitution, and were corrected for the buoyancy of the air. A counterpoise was always used of the same size and material as the vessel to be weighed, and the vessel was always left near the balance for several hours before weighing.

Dehydration of the Sodium Metavanadate.—The powdered substance, when heated for several hours at 385°, still retains about 0 05 per cent. of moisture. It melts at a dull red heat, and on cooling forms white radiating crystals, slightly hygroscopic. If heated for a time at bright redness, it appears to lose weight continuously, although very slowly; by fusion at dull redness, however, it is easy to get a constant weight.

Specific Gravity of Anhydrous Sodium Vanadate.—The specific gravity of the fused salt was determind by putting a known weight of the substance into a pycnometer, filling the pycnometer with alcohol and weighing it.

The weight of alcohol required to fill the pycnometer was 14.593; the weight of sodium vanadate used was 5.4375, and the weight of the sodium vanadate and alcohol required to fill the vessel was 18.4335. Therefore the weight of alcohol displaced by the vanadate was 14 593 — (18.4335—5.4375) = 1 600. Since the specific gravity of the alcohol was 0.82, the specific gravity of the sodium vanadate is 5.437/1.600 × 0.82 = 2.79.

Corrections for Buoyancy of the Air.

The correction for the weight of one gram of sodium vanadate is equal to the weight of 1 cc. of air multiplied by the difference between the volume of 1 gram of vanadate and 1 gram of weights. The temperature varied from 20 to 30° in the progress of the experiments, but the pressure did not vary much from 750 mm., so the correction was calculated for 25° and 750 mm. The weight of 1 cc. of air under these conditions is 0.00117, the volume of 1 gram of vanadate is 0.358 and of 1 gram of brass 0.119; therefore the correction for 1 gram of vanadate is 0.00117 × (0.358–0.119) = +0.00028. For 1 gram of sodium chloride, using the accepted value 2 14 for the specific gravity, the correction is 0.00117 (0.468–0.119) = +0.00041.

Experiments and Results.

Several modifications of the vessel used to contain the sodium vanadate were tried before a satisfactory form was found.

It was found impossible to remove all vanadium from the vessel unless a fresh surface of material was frequently exposed to the action of the gases. This could be done only by moistening the substance and again drying it. To admit of this treatment, a flask, G, of the form shown in the figure, was designed; the flask and inner tube were made of quartz. The small bulbs prevent loss of sodium chloride by decrepitation.

In order to get the weight of the sodium vanadate, it was fused in a platinum capsule and rotated just before solidifying, so as to spread the substance in a thin layer; the total weight of capsule, vanadate and a platinum rod was then taken. By means of the platinum rod, the vanadate was then broken up and as much as possible transferred to the weighed quartz flask, which was held vertically. After again heating the capsule and rod, the loss in weight indicated the amount of sodium vanadate transferred to the flask.

The apparatus was now adjusted and hydrochloric acid and chlorine were passed through the quartz vessel while it was heated. The quartz dish H was heated by a Bunsen burner, and two other burners were arranged above the vessel, so as to radiate sufficient heat downward; a small flame was also placed under the exit tube and thus any crawling of material was prevented.

When as much as possible of the vanadium had been removed, a little water was added to the substance in the flask, and it was again dried in the stream of gas, being rotated at the last in order to spread the material over the inner surface of the vessel.

In this process, the sodium chloride first dissolved in the water, leaving the vanadium; then, as the hydrochloric acid was passed in, the vanadium dissolved and the sodium chloride crystallized out. As the liquid evaporated, the vanadium compound was left on the surface, where it could be attacked by the gases.

After three or four of these treatments, the vanadium could all be driven out of over nine grams of vanadate, leaving a perfectly white residue which gave no indications of vanadium by the aniline test.

The aniline test was worked out by Witz and Osmond,[1] and is of value in estimating very small quantities of vanadium. It depends on the fact that vanadium salts are easily oxidized and reduced, and therefore can act as oxygen carriers.

If a solution of potassium chlorate is added to a solution of aniline hydrochloride, heated to boiling, and allowed to stand at room temperature, no coloration appears. If, however, a trace of vanadium is present, a color appears, varying from light yellow to black, according to the amount of vanadium present. More than a trace of vanadium will cause a precipitate of aniline black. The sensitiveness is increased by the presence of a small quantity of dilute hydrochloric acid, but a larger quantity will cause a precipitation of aniline black, even when no vanadium is present.

In making this test, a standard vanadium solution was used, containing about 0.0001 gram V_2O_5 to 1 cc.; this was used for color comparison as in the Nessler test for ammonia, and in neutral solution was about as delicate.

The time required to get all the vanadium out was about thirty hours of actual heating, and seemed to be independent of the quantity of vanadate used. The white color of the sodium chloride proved to be a very good indication of its freedom from vanadium.

---

[1] *Bull. soc. chim.*, (2) **45**, 309.

An attempt was made to use a Jena glass flask, but it cracked at a critical moment, so a quartz flask with straight neck and Jena glass inner tube was next tried. Only one experiment was completed, because the inner tube fused in contact with the quartz, when the sodium chloride was finally heated to fusion; the results of this experiment are recorded under (1) in the table. The material used was Sample A.

It was necessary to send to Germany and have two quartz flasks made of the form shown in the figure.

An advantage of the use of the quartz apparatus is that the sodium chloride could be heated to complete fusion in the vessel and all moisture thus removed. It was found that the fusion caused practically no loss by volatilization, and a quite definit weight for the salt could be obtained. The losses on heating were about as follows: The flask and salt were weighed after fusion of the salt on the edges. After complete fusion, there was a loss of 0.0012 gram. After again fusing it for several minutes to the highest temperature of the blast lamp, there was a further loss of 0.0001, or sometimes 0.0002 gram. The last weight was taken as correct. The bulb on the inner tube nearly closes the outlet to the flask, when it is held vertically, and this evidently prevents loss by volatilization.

Another quartz apparatus of the same size and shape was used as a counterpoise, the difference in weight by substitution of the flask and counterpoise being taken; on the opposit pan of the balance a quartz dish of the same weight was used as a tare. It was necessary to leave the apparatus in the balance case for several hours before the final weighing was taken. On being transferred from desiccator to balance case, the flasks seemed to lose about 0.001 gram in weight in the first hour; after that the weight would be practically constant. The loss was undoubtedly due to the fact that the flasks were filled first with the dry air of the desiccator and then with the moister air of the balance case.

After getting the final weight of the flask and fused sodium chloride, the flask was rinsed out with distilled water, heated with a blast lamp, and again weighed. The difference in weight is recorded in the table as "loss on rinsing."

On the second experiment, there was a slight increase in weight of the flask, and at the same time a slight greenish yellow coloration appeared in the neck. The yellow color remained through all the experiments; and the weight of the flask remained practically constant except in experiment IV.

In experiment IV there was a considerable gain in weight of the flask and an increase in the yellowish color on the neck. The increased color persisted until the inner surface of the neck of the vessel had been rubbed with a cloth moistened with various reagents, such as acids, ammonia and caustic potash. This treatment caused the yellow color to fade somewhat and the weight of the flask to become normal.

On heating the neck of the flask with the blast lamp, the color would travel around to the opposite side from the flame, but could not be driven away.

Our explanation is that some vanadium vapors were taken up by the quartz in the neck of the apparatus, where the heat was much less than in the body.

By taking the loss of weight on rinsing, this would not cause any error in the results.

The solution obtained by rinsing out the vessel showed a very slight turbidity which looked like silica. In one case, a few shining scales could be noticed, which evidently came from the quartz flask. This was undoubtedly due to the contraction of the fused sodium chloride on cooling; although it was spread as thin as possible, it always broke apart with considerable crackling.

The solutions obtained in the last five experiments were filtered through a small filter whose ash weighed 0 00003 gram; after ignition in a platinum crucible the weight of the silica was obtained.

Just how to apply this correction was somewhat of a puzzle. If the silica came from the quartz vessel, its loss was evidently balanced by other material absorbed, for the weight of the vessel did not decrease, and yet in one case a slight corrosion of its walls was visible. It was finally decided to assume that the silica came from the flask, and subtract its weight from the "loss on rinsing." If part of it came from the sodium vanadate, our method of correction would not be far wrong, since the silica would affect the observed weight of sodium chloride over twice as much as that of the vanadate.

In practically all cases the filtrate from the silica was tested for vanadium by the aniline test, and any trace thus indicated was subtracted from the "loss on rinsing."

The results of five experiments are given in the table in the order in which they were obtained.

Average is 50.967 ± 0.006. The atomic weights of sodium and chlorine were assumed to be 23 00 and 35 46, respectively.

The sample used in V had been the most carefully prepared of any of the series, and the amount of material used was so large that the percentage error in the weighing of the sodium chloride would be considerably diminished. So perhaps this should be given more weight in making up the average.

Number. Date. Sample.	I. 1909. A.	II. 1910. B.	III 1910. B.	IV. 1910. E.	V. 1910. F.
Color of fused vanadate	Colorless	Nearly colorless	Nearly colorless	Nearly colorless	Colorless
Wt of $NaVO_3$ in air .	4.8550	5.6388	4.4251	5.7789	9.4875
Correction for buoyancy of air.	0.0014	0.0016	0.0012	0.0016	0.0027
Wt. of $NaVO_3$ in vacuum.	4.8564	5.6404	4.4263	5.7805	9.4902
Excess wt. of counterpoise over flask—before.	—0.8609	2.1286	2.1282	2.1283	2.1283
Excess wt of counterpoise over flask—after.	....	2.1282	2.1283	2.1257	2.1282
Excess of wt. of flask, and NaCl over counterpoise..	3.1876	0.5746	–0.0062	0.6450	2.4187
Loss of wt. on rinsing .	...	2.7028	2.1221	2.7707	4.5469
Wt. of silica...	...	0.0006	0.00094	0.0008	0.0009
Wt. of vanadium left. .	None	None	0.00006	0.00005	0.00005
Wt. of NaCl in air. .	2.3267	2.7022	2.1211	2.7699	4.5460
Correction for buoyancy of air	0.0010	0.0011	0.0009	0.0011	0.0018
Wt. of NaCl in vacuum. .	2.3277	2.7033	2.1220	2.7710	4.5478
Mol. wt. of $NaVO_3$ . .	121.966	121.976	121.946	121.952	121.997
Atomic wt. of vanadium.	50.966	50.976	50.946	50.952	50.997

The experiments had to be interrupted at this point, but it is intended to make another series at some future time, using from seven to ten grams of vanadate in each experiment.

Conclusion.

This series of fairly concordant results, obtained with material prepared in several different ways, proves that sodium metavanadate is a definit and stable compound, and that it can be prepared free from excess of alkali and from acid vanadates.

The errors which would make our calculated values for the atomic weight too high are: Presence of acid vanadate, silica, or moisture in the fused sodium vanadate, and loss of sodium chloride by decrepitation or volatilization.

The errors which would make the calculated value too low are: Presence of excess of alkali in the fused vanadate, and presence of moisture in the sodium chloride.

It is hard to see how our calculated value can be too low, since correction has been applied for silica and for any vanadium remaining in the sodium chloride and the moisture must have been completely removed.

This work, in connection with that of Prandtl and Bleyer, therefore indicates that the value for the atomic weight of vanadium is about 51.0 instead of 51.2.

The writer wishes to express his thanks to Prof. W. B. Schober, of Lehigh University, for the use of the laboratory and valuable apparatus in part of this work. The valuable assistance of Mr. F. B. Kingsbury and Mr. C. A. Pierle is hereby acknowledged.

PHILADELPHIA, PA.

[COMMUNICATION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

A METHOD FOR DETERMINING THE MOLECULAR WEIGHTS OF DISSOLVED SUBSTANCES BY MEASUREMENT OF LOWERING OF VAPOR PRESSURE.[1]

BY ALAN W C MENZIES

Received October 26, 1910

Among the methods available for measuring the molecular weights of substances in solution, the cryoscopic and the ebullioscopic methods are most commonly used. The method of directly measuring the lowering of vapor pressure due to the dissolved substance has not been commonly applied for molecular weight determination owing, perhaps, to the difficulty of obtaining trustworthy values of vapor pressure by the static method, even when elaborate apparatus is employed. It is proposed in the present paper to describe an apparatus and procedure by means of which, without any thermometer, molecular weights may be simply determind in the laboratory by static measurement of vapor pressure, with an accuracy at least equal to that obtained by the ebullioscopic method.

In 1858 Wullner,[2] working with aqueous solutions, found the lowering of vapor pressure roughly proportional to the concentration of the dissolved substance. The fact that workers[3] in this field confined their observations to aqueous solution of salts, which are abnormal, prevented the recognition of the underlying regularities until as late as 1886–7. Raoult's work[4] of that epoch is the basis of the present-day cryoscopic and ebullioscopic methods.

Raoult used a barometer tube, static method for measuring vapor pressures of solvent and solution. As with all static methods, chief among the sources of error are (1) the difficulty of completely eliminating gaseous and volatil impurities, and (2) the variation of the superficial concentrations of solutions due to evaporation and condensation. Even were it sufficiently accurate, Raoult's apparatus is too cumbrous for every-day use in molecular weight determination.

---

[1] Read before the American Chemical Society, Dec 31, 1909.

[2] *Pogg. Ann.*, **103**, 529 (1858); **105**, 85 (1858); **110**, 564 (1860).

[3] For example, Pauchon, *Compt. rend.*, **89**, 752 (1879); Tammann, *Wied. Ann.*, **24**, 523 (1885); Emden, *Wied. Ann*, **31**, 145 (1887).

[4] *Compt. rend.*, **103**, 1125 (1886); **104**, 976, 1430 (1887); **107**, 442 (1888); *Z. physik. Chem.*, **2**, 353 (1888); *Ann. chim. phys.*, [6] **15**, 375 (1888).

Air-current or air-bubbling dynamic methods for vapor pressure measurement[1] always appear promising but, perhaps on account of their inflexibility hitherto, they have not come into general use for the purpose under consideration.

After evolving his form of freezing point apparatus, Beckmann[2] turned his attention to devising a workable method of molecular weight determination by vapor pressure measurement. He discarded those methods which he tried, however, in favor of his well-known ebullioscopic method. With the benefit of the experience of these earlier workers, Biddle[3] described a vapor pressure apparatus for molecular weight determination; this, however, is somewhat complex, requires the use of a thermostat, and is applied only to the very volatil solvents, ether and carbon bisulphide.

The Apparatus.[4]—As will be seen from Fig. 1, the apparatus here proposed consists of a jacket, in which the solvent is boiled, attached to a small reflux condenser, and an inner "test-tube" furnished with a pressure gage tube and a glass stopper. The dimensions of the jacket are, length 27 cm., diameter 3.5 cm.; those of the inner "test-tube," total length 30 cm., diameter 2.3 cm. The side tube leading from the jacket to the condenser is of glass of 1 cm. bore, so that the solvent may boil under a pressure no greater than barometric. The connection may be made with an 8 cm. length of rubber tubing, furnished with a screw clip. When the glass stopper is removed and the clip closed, the vapor of the liquid boiling in the jacket is obliged to escape by blowing through the gage tube, which is open at both ends, into the test tube. The narrow (6 mm.) U-shaped side tube attached to the jacket returns the cold condensed vapor from the condenser to the lower portion of the jacket, thus avoiding chilling of the upper portion of the test tube. The latter is graduated in cubic centimeters from 15 cc. upwards, and the gage tube (diam. 5 mm.) in millimeters of length (total about 140 mm.) from above

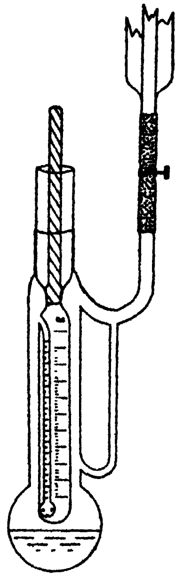


Fig. 1.

---

[1] Cf. Regnault, *Ann. chim. phys.*, [3] 15, 129. Tammann, *Wied. Ann.*, 35, 322. Walker, *Z. physik. Chem.*, 2, 602. Will and Bredig, *Ber.*, 22, 1084. Carveth and Fowler, *J. Physic Chem.*, 8, 313 Kahlenberg, *Science*, 22, 74. Earl of Berkeley and Hartley, *Proc. Roy. Soc. London*, 77, 156. Perman, *Proc. Roy. Soc.*, *London*, 72, 72. Lincoln and Klein, *J. Physic Chem.*, 11, 318. Krauskopf, *Ibid.*, 14, 489.

[2] *Z physik. Chem.*, 4, 532.

[3] *Am. Chem. J.*, 29, 341

[4] This may be had from the Central Scientific Co., 349 W. Michigan Street, Chicago, Ill.

downwards. The two sets of graduations are readable from aspects at right angles to each other, so as to avoid confusion. At its foot, the gage tube is blown into a small bulb in which are pierced a number of holes to distribute the vapor as it issues. A glass stopper, with a glass-rod handle (length 12 cm.), fits the constricted neck (diam. 12 mm.) of the test tube, while the test tube itself fits into its jacket by a ground joint. The purpose of the jacket is to maintain the test tube and its contents at a constant temperature—the boiling point of the solvent—while the purpose of the test tube is to contain the solution whose vapor pressure is being measured. The pressure measurment is made in terms of the difference of level of the solution in the gage tube and the test tube, that is, in terms of millimeters of a liquid of low density compared to mercury. Differences of pressure that are small in terms of millimeters of mercury may therefore be measured with accuracy, and this permits of the use of very dilute solutions.

The Procedure.—The procedure followed in making a molecular weight determination may properly be described in some detail. The bulb of the jacket is charged two-thirds full with the pure solvent, the empty "test tube" replaced in position, and the liquid boiled with a small naked flame for ten minutes under its reflux condenser, in order to expel dissolved gases. The flame is then removed, the test tube taken out and charged two-thirds full with the boiled-out liquid from the jacket and replaced in position with its stopper left out. The liquid in the jacket is again boiled for a minute to expel air, after which the screw-clip is closed sufficiently to cause a vigorous bubbling of vapor through the liquid in the test tube. After this "blowing-through" process has continued two or three minutes, the stopper is warmed up by inserting it obliquely in position. Vapor can still escape, but the condensed liquid collects to form several drops above the stopper. When this has taken place, the stopper is pushed home, the liquid above it serving to make the joint gas-tight, and at the same moment the screw clip is fully opened. At this stage, the temperature of the liquid in the test tube is slighly higher than the boiling point, because the liquid in the jacket has been boiling under a slightly increased pressure in order to cause the "blowing-through." The apparatus must therefore be allowed to stand for a few minutes until the temperature of the vapor chamber adjusts itself to the true boiling point of the solvent. As the jacket is clamped loosely only at its neck, the apparatus may be shaken occasionally with a jerking motion, by way of stirring.

If the dissolved gases have been removed, and if the solvent is perfectly pure and dry, the relative levels of the liquid in the test tube and gage tube will now be precisely the same as they were before the stopper was inserted; unless the solvent has been very carefully purified, however, such theoretical perfection will not be quite attained. It is obvious that the liquid in the gage tube stands somewhat the higher of the two, on account of capillarity, as shown in Fig. 2 (*a*). This reading of difference of level is taken as the zero reading, and affords an excellent test of the adequate purity of the solvent. Should the zero reading be unsatisfactory, the process of blowing-through may be repeated until at least constant results are obtained. All readings are conveniently made with the help of a small lens.

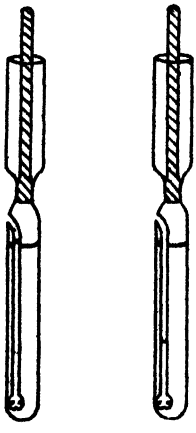


Fig. 2.

On removing the stopper, the substance may now be introduced in the form of weighed pastils, or otherwise. Solution is assisted by a gentle "blowing-through," which is necessary also to remove air. When the liquid is judged to be homogeneous and air-free, the stopper is again inserted, exactly as before, and the apparatus allowed to stand with shaking every half minute or so. At this stage the shaking, which should jerk the solution so as to wash the upper portion of the vapor-chamber walls, is very essential if surface films of abnormal concentration are to be avoided. By the circulation it causes, shaking also hastens the cooling of the central portions of the solution to the boiling point of the pure solvent. At no time, of course, must the boiling of the pure solvent in the jacket be interrupted. In about ten minutes, when the difference of level (see Fig. 2 (*b*)) after successive shakings has become constant, the reading is made and corrected by the zero reading.[1] The stopper is now removed and the volume of the solution read off, the liquid above the stopper being first removed by filter paper.

Further measurements may be made at different concentrations, either by adding more solute or else by blowing through for some time and so adding more pure solvent. Such further measurements are, however, usually unnecessary, since, with the very dilute solutions employed, the values first obtained are hardly improved by the method of extrapolation to infinit dilution.

In the case of solvents as volatil as carbon disulphide, a common test-tube filled with cold water may be inserted in the projecting upper portion of the "test tube" during the blowing-through process, if necessary to assist condensation. If, for any solvent, the rubber connection is considered objectionable, a glass stopcock[2] of large bore may take the place of the screw clip, and the use of rubber be entirely avoided.

[1] If the apparatus be allowed to stand over a couple of minutes without shaking a slow change of level appears, caused by distillation within the vapor chamber towards the stopper.

[2] To regulate more easily the passage of small quantities of vapor, notches should be filed at the sides of the holes piercing the stopper of the cock.

Calculation of Results.—From the well-known relationship

$$p - p' = P\sigma/(\rho - \sigma)$$

where, at any temperature, p is the vapor pressure of the pure solvent, p' that of the solution, P the osmotic pressure of the solution, ρ its density and σ the density of the vapor under the pressure[1] p, one may, in the case of very dilute solutions, by assuming van't Hoff's law and making the appropriate substitutions for P and σ, deduce for a barometric height of 760 mm.:

$$p - p'(\text{in mm. mercury}) = n \cdot m \cdot 760/1000\ (\rho - \sigma)$$

where n is the number of dissolved moles per liter of solution, and m is the molecular weight of the solvent in the gaseous state. In millimeters of solution partially counterpoised by vapor of density σ, this would become, if $n = 1$,

$$p - p'\ (\text{in mm. solution}) = m \cdot 760 \cdot 13.59/1000 \cdot (\rho - \sigma)^2$$

where 13.59 is the density of mercury at 0°. By assuming that $\rho - \sigma$ is equal to the density of the pure solvent[2] at its boiling point, one may thus calculate for a series of solvents the values of $K_{760} = p - p' =$ the lowering of vapor pressure in mm. of boiling solvent that would be caused by the presence of one mole of non-volatil solute in one liter of solution, the barometer being normal. The values of K_{760} for some of the common solvents are as follows:

Solvent.	Density at boiling point	K_{760}.
Benzene	0.8149	1214
Alcohol	0.7389	871.5
Water	0.9587	202.5
Chloroform	1.4101	620.4
Acetone	0.7518	1061
Ether	0.6968	1577
Carbon disulphide	1.2223	526.6
Ethyl acetate	0.8302	1320
Ethylene dibromide	1.9423	514.6

If desired, the actual value for ρ for any solution may be found directly by making a weighing of the test tube and its contents, in addition to reading off the volume of the solution, and σ may be calculated. This, however, is unnecessary for the ordinary purposes of molecular weight determination, and was not done in the examples given below.

---

[1] Should $p - \frac{p - p'}{2}$ be preferred, since with this apparatus $p - p'$ has values from about 3 to 7 mm. of mercury, the constants K would become from one-quarter to one-half per cent. smaller.

[2] At their boiling points under 760 mm., σ for carbon bisulphide, benzene, chloroform and alcohol has a value about 0.24, 0.33, 0.31 and 0.32 per cent., respectively, of ρ. If the densities of the solutions used in this apparatus exceeded the density of the pure solvent by precisely these amounts, no error would be committed by the assumption made.

The change of ρ due to a change of boiling point of the solvent caused by a barometric divergence of 10 mm. from the normal is of the order of 1 part in 1000, and is therefore negligible.

Knowing the value of K_{760} as given above, the molecular weight may be calculated from the formula

$$M = 1000\, W \cdot K \cdot B / L \cdot V \cdot 760$$

where W is the weight of solute added, L is the measured lowering of pressure in mm., V is the volume of the solution in cc., and B is the barometric height.

Examples of Results.—The table below gives examples of the results obtained with six solvents. The benzene was the crystallizable, thiophene-free product of Kahlbaum and was dried and distilled over sodium The carbon disulphide was distilled once. The alcohol, also Kahlbaum's, was dried and distilled over barium oxide. The chloroform was freed from alcohol by washing with chromic acid mixture and dried over calcium chloride. A quantity of acetone, from the disulphite compound, was distilled once with a Hempel's fractionating tube, and the first portion of the distillate taken. The solutes were also the preparation of Kahlbaum, and were used without further purification other than drying. In the table, the results of Beckmann[1] and of Walker and Lumsden[2] are added for comparison. The figures refer to the lowest and the highest concentrations which they used:

Weight of solute.	Volume of solution.	Lowering observed.	Molecular weight found	Beckmann found	W & L found.
		Solvent, Water.			
		Potassium Nitrate, 101.			
0 611	36.7	57.1	56.9		53
0.611	37.7	56.9	57.0		
0.611	38.2	56.4	56 6		
		Sodium Chloride, 58.5.			
0.351	38.0	56.2	32.5		32
0 579	40.4	84.4	33.3		
0.488	33.8	84.4	33.4		
		Solvent, Benzene.			
		Naphthalene, 128.			
0 3115	48.1	60.1	128.6	141–144	139–141
0.5118	49.1	105.2	127.5		
0 3237	46.1	65.2	128.0		
0.5092	46 8	101.6	127 3		
		Anthracene, 178.			
0.336	45.0	48.5	186.2	192	184–187

---

[1] *Z. physik. Chem.*, **6**, 437.

[2] *J. Chem. Soc.*, **73**, 502.

Weight of solute.	Volume of solution.	Lowering observed.	Molecular weight found.	Beckmann found.	W & L. found.
Solvent, Carbon Disulphide.					
Naphthalene, 128.					
0.4166	43.2	32.2	126.3	131–141	
0.7632	43.8	69.6	128.6		
1.0386	44.3	95.7	125.9		
Anthracene, 178.					
0.8504	44.7	55.0	178.2	175–185	
1.4255	46.5	90.8	173.9		
1.8503	51.0	109.0	171.4		
Solvent, Alcohol.					
Naphthalene, 128.					
0.425	37.0	64.1	153.7	148–155	147–157
Mercuric Chloride, 271.					
1.058	42.0	83.0	260.2	263–271	261–263
Solvent, Chloroform.					
Naphthalene, 128					
0.447	43.1	47.5	133.4	128–133	125–126
0.865	43.5	93.6	129.9		
0.804	44.7	81.5	136.0		
Solvent, Acetone.					
Naphthalene, 128					
0.3264	41.9	60.4	133.2	128–155	
0.3424	39.6	68.6	131.8		
0.3424	39.7	68.6	131.9		
0.4874	40.8	92.2	133.5		

For the following determinations I am indebted to Mr. Severin Gertken, who was without previous experience of molecular weight determination by any method:

Weight of solute.	Volume of solution	Lowering observed.	Molecular weight found.	Beckmann found.	W. & L. found.
Solvent, Carbon Disulphide.					
Benzil, 210.					
1.851	47.4	98.9	206.5	217	
Benzophenone, 182.					
1.069	47.2	59.6	195.9	182–187	
1.069	47.3	59.7	196.3		
Naphthalene, 128.					
0.988	51.6	77.4	127.6	131–141	
Solvent, Benzene.					
Benzil, 210.					
0.650	50.3	26.1	203.0	216–256	
Ethyl Benzoate, 150.					
0.662	53.2	90.5	164.5	163–172	

Weight of solute.	Volume of solution.	Lowering observed.	Molecular weight found.	Beckmann found.	W. & L. found.
		Solvent, Water.			
		Boric Acid, 62.			
1 201	43 0	90 7	61.6	64.6–66 9	
1.147	46 7	79.2	62.1		
1.147	46.3	81.2	61.4		
		Potassium Chloride, 74.6.			
1.001	44.8	102.2	44.2		
1.001	45.0	103.1	43.2		
1.001	45.2	102 4	43.3		

In the values found for the molecular weight, the first decimal place has been retained for purposes of comparison, but it is of little value.

Comparison with Ebullioscopic Methods.—That this method possesses greater potentialities for accuracy than the ebullioscopic method will be admitted when it is considered that an elevation of boiling point of 0.1° corresponds to a measured lowering of vapor pressure of, for example, 37, 55 and 37 mm., respectively, for water, alcohol and benzene. It should therefore be possible, with like accuracy, to employ. with this method, much more dilute solutions. This leads to the consideration of a chief source of error of the ebullioscopic methods when the more dilute solutions are employed, namely, change of boiling point due to change of barometric pressure during the experiment. To cause an error of temperature of 0.05°—fifty per cent. of the quantity measured in the case above considered—the barometer need change only 1 36 mm., 1 5 mm. and 1.2 mm., respectively, for water, alcohol and benzene. Such barometric changes affect the results of the method here described scarcely at all, since the temperature of the jacket varies proportionally, and thus automatically corrects this error. Change of barometer influences the result only by slightly affecting the constant K, which depends on absolute barometric height, as indicated above. It may be pointed out that, in the case of the ebullioscopic methods, the constant used is customarily obtained experimentally and not by calculation from theory as in the case of the method here outlined.

The time occupied in a first determination by this method may be thirty to forty minutes, including the necessary weighing. In discussing the Beckmann boiling point method, H. Biltz[1] states that 'it usually requires one hour, but often two, and sometimes, indeed, several hours, to obtain a constant temperature in the boiling vessel.' How much of this trouble is due to slow change of zero of the thermometer is difficult to say. Presumably very little, as the Landsberger type of apparatus is much more expeditious, in the form, for example, devised by McCoy.[2]

---

[1] "Pract. Methods for Determining Molecular Weights," Transl. by Jones and King, p. 155.

[2] See *Am. Chem. J.*, 23, 357 (1900).

Apropos of the thermometer, it will be recalled that a Beckmann thermometer whose degree is correct at zero is 3 6 per cent. in error[1] at 100°. Accordingly, whenever a Beckmann thermometer is employed at temperatures far from that at which its degree is correct, a correction for this error becomes necessary, although it is frequently omitted. The absence of any thermometer in the present apparatus simplifies slightly the reading of the volume of the solution; when a thermometer is present, it must first be removed.

In this apparatus, the 1 cc. graduations have a distance apart of about 2.8 mm., which makes the estimation of tenths satisfactory.

A considerable error is incident to both Berkmann and Landsberger methods when the correction for varying head of liquid above the thermometer bulb is neglected. Such an error does not here appear, for it is on the measurement of precisely such heads of liquid that the present method is based.

The use of a reflux condenser avoids the errors caused by change of temperature due to fractionation of the jacketing liquid inherent in the Landsberger method and its modifications.

The Identity of Vapor Pressure as Determined by the Static and by the Dynamic Methods.—It was tacitly assumed above that the statically determind vapor pressure of a pure liquid at its boiling point, determind dynamically, should be precisely the pressure under which the liquid boiled. In other words, it was taken for granted that if p is measured statically for any particular t, the same t will be arrived at dynamically by a boiling point measurement if p be the same. As is well known, however, it was by no means always agreed that this is the case.[2]

The apparatus here described is well adapted for testing the facts. The vapor pressure of the pure solvent in the test tube is a "static" vapor pressure, and is measured at the dynamically attained temperature of the vapor from the pure solvent boiling in the jacket. The pressure comparison is made by a differential gage of a liquid of low specific gravity, instead of, for example, by the difference of level of two mercury columns, one of which has a small depth of another liquid lying on its surface. With benzene, for instance, a pressure difference of 0.5 mm. of mercury, obtained in other methods by subtraction of much larger numbers of mm. and the application of not a few corrections, is, by this method, seen directly on a single small apparatus as a difference of level of 8.3 mm. of benzene at its boiling point (which is the manometer liquid). More important than simplicity of the pressure reading, however, is the possibility of boiling out dissolved gases until constant results are obtained; because failure to realize this possibility has been a chief cause of inconsistences in all measurements by the static method.

---

[1] *Z. Instrum.*, 1896, 202.

[2] References to the extensive literature of the controversy on this subject may be found in Ostwald's *Lehrbuch*, Vol. I, 308.

As, therefore, it seemed of interest to determin whether any small difference could be detected between static and dynamic results, the experiment was made with pure water, alcohol and benzene. The following figures refer to benzene, which had recently been distilled over sodium, but was not boiled out in the jacket. The differences of pressure, Δp, are in mm. of benzene at its boiling point, while the times, T, refer to the number of minutes of the "blowing-through" process:

Δp	6 3	2 5	0 9	0.1	0.1
T	5.0	6 0	8 0	10.0	12.0

The zero reading was that found when the stopper was removed. It will be seen that the difference of pressure finally observed was not larger than the limits of the error of observation.

It was shown in a similar way that, if any difference exists between the vapor pressure at the boiling point as measured dynamically and statically of the liquids water and alcohol, then such difference does not exceed 0.01 mm. of mercury.

Purpose and Scope.—In the present paper, the purpose has been to describe a molecular weight apparatus and its every-day application in cases where the greatest refinement is not aimed at. When opportunity offers, it is proposed to carry the measurements to their highest accuracy, and to make such applications of the method as promise to be most productive.

[Communications from the Laboratories of General and Physical Chemistry of the University of Chicago.]

A CONVENIENT FORM OF APPARATUS FOR THE MEASUREMENT OF THE VAPOR DENSITIES OF EASILY VOLATIL SUBSTANCES.[1]

By Alan W. C. Menzies.

Received October 26, 1910

By the very slight modification here explained, the apparatus described in the preceding paper may be simply adapted for the rapid and accurate measurement of vapor densities of easily volatil substances.

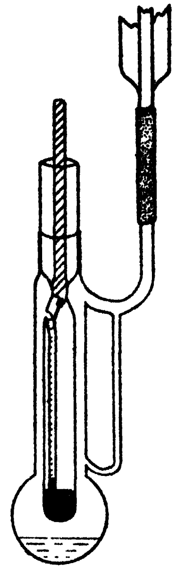
The principle employed is that of the measurement of the increase of pressure that occurs when a known weight of substance is introduced into a closed vessel at constant temperature, high enough to completely volatilize the substance.[2]

The Modification Required.—The closed chamber is provided by the "test-tube" of the former apparatus, which is the inner tube in the figure. This is closed below by pouring in from six to eight cc. of mercury. This mercury serves at the same time the purpose of manometer liquid, indicating by its rise in the graduated narrow gage tube the increase of pressure within the test tube.

---

[1] Read before the American Chemical Society, July 15, 1910.

[2] For other work in this field cf. Gibson Dyson, *Chem. News*, 55, 88 (1887); Bleier and Kohn, *Monatsh.*, 20, 909; 21, 575; Lumsden, *J. Chem. Soc.*, 83, 342; Blackman, *Chem. News*, 100, 13; etc.



The substance is weighed off in bulblets whose attached capillaries, 2–3 cm. in length, are sealed off before the final weighing. In order to attach the bulblet to the stopper of the test tube, the latter must be provided with a hole of about 1.5 mm. diameter and 5–6 mm. length. This hole may be drilled in the glass stopper, or else *added* by fusing to the lower end of the stopper a short length of thick-walled tubing of 1.5 mm. bore. The point of the bulblet's capillary can now be fixed in this hole by stuffing with a few shreds of dry asbestos. The hole should be oblique, in order that the neck of the bulblet may be broken by rotating the stopper in such a way that the bulblet is forced against the top of the gage tube (see figure). It is evident that the presence of this small hole in no wise unfits the apparatus[1] for its original purpose.

The Procedure.—The bulb of the outer jacket is charged one-third full with a liquid of suitably high boiling point, which is caused to boil steadily, the vapor thus serving to jacket the whole of the closed portion of the test tube. It is most convenient in practice to find a constant for the apparatus, at the temperature used, by volatilizing a known weight of a standard liquid, such as benzene, rather than to calculate the vapor density from measurements of the volume of the closed chamber and of the temperature. A quantity of benzene suitable to give a rise of mercury level of about 100 mm. is, therefore, sealed and weighed in a bulblet. The smaller the bulblet that will hold the requisite quantity of liquid, the better. The neck of the bulblet is then prepared for easy breaking by one or two scratches from a file. The tip of the capillary is inserted in the hole in the stopper, and the latter, after suitable lubrication, placed cautiously in its position. As the air surrounding the cold bulblet becomes warmed, the mercury rises a few mm. in the gage tube and in 5–6 minutes has reached a constant level, which is read off on the engraved scale of mm. Its position is shown in the figure. The stopper is now rotated so as to snap the neck of the bulblet, which falls on to the surface of the mercury. At the same instant the mercury in the gage tube shoots up, and reaches a constant level in a few seconds. The amount of rise is observed, and is corrected by adding the amount of the simultaneous slight fall of mercury level in the test tube.[1] From the three data (1) weight of benzene taken, (2) known molecular weight of benzene, (3) rise in mm., is calculated a constant for the apparatus, *K*, which is the rise in mm. that would be caused by the volatilization of one gram-molecular weight of any substance in this apparatus at this temperature. Having obtained this constant, the unknown molecular weight of any substance may be calculated by substituting the measured rise, *R*, and weight taken, *W*, in the formula

---

[1] The apparatus, with the modified stopper, may be had from the Central Scientific Co., 349 W. Michigan Street, Chicago, Ill.

$$M = W \cdot K / R.$$

After each measurement, the stopper is removed and a current of air aspirated through the test tube for a few seconds by introducing into it the end of a tube connected with the water pump. Several of the broken bulblets may be allowed to accumulate in the apparatus.

Examples of Results.—The measurements recorded below, including the time necessary for the weighings and for finding the constant of the apparatus, were completed in a period of three hours. The jacket contained boiling toluene. The substances whose molecular weights are determined were the preparations of Kahlbaum, each dried and purified by distillation. The chloroform was previously freed from alcohol by washing with chromic acid mixture. Every result obtained is given:

Substance.	Weight taken.	Rise in mm.	Log. *K*.	Molecular weight.	
				Found.	Normal.
Benzene....	0.0238	16.5	5.5820	..	78.05
	0.0205	100.5	5.5827	....	....
Ethyl iodide....	0.0429	104.7	5.5824	156.7	156.0
	0.0328	80.5		155.8	...
Carbon disulphide...	0.0262	132.1	...	75.8	76.1
	0.0180	90.7	....	75.9	....
Chloroform........	0.0312	99.9	....	119.4	119.4
	0.0347	110.0	...	120.6	....
Methyl iodide......	0.0328	87.4	....	143.6	141.9

For the following determinations, I am indebted to Mr. R. D. Mullinix, who was without previous experience of vapor density measurements by any method, and who, indeed, first learned to weigh accurately in order to make these determinations. The jacket contained commercial xylene, b. p. 137.8°. Every determination made by Mr. Mullinix, other than his preliminary ones, is recorded:

---

[1] The value of this correction for a given rise of mercury in the gage tube having been determined once, the values for other cases are thereafter obtained by simple proportion.

Substance.	Weight taken.	Rise in mm.	Log. *K*.	Molecular weight.	
				Found.	Normal.
Benzene .	0 0215	112.0	5 6091	..	78.05
	0 0210	110.3	5 6126	..	...
	0 0211	110 1	5 6098	..	...
Toluene... ..	0 0246	110 2	5 6105	91.1	92.1
	0 0231	100.2	....	93.2	
	0 0248	108 0	.	93.6	
Acetone . .	0 0158	108 1		59 6	58.0
	0 0157	108 9		58 9	.
	0 0156	113 8		55 9	...
Chlorobenzene	0 0276	100 1		112.4	112.5
	0 0270	95 5	.	115.3	..
	0 0266	89 1		121 8[1]	..
Ethyl iodide ..	0 0418	108 6		157 0	156 0
	0 0409	107.1		155 7	. .
	0 0433	not completed --stopper leaked			...
Pyridine	0 0216	108 9	.	80.9	79.0
	0 0238	124 0	.	78.2	...
	0 0233	120 7		78 5	...
Acetic acid[2].... .	0 0140	92.6	.	61 7	60.0
	0 0162	106 7	.	61 9	

As an example of the application of this apparatus to a special problem, the percentage composition of a binary mixture of substances of known molecular weight may be found. For this purpose, the solubility of carbon disulphide in methyl alcohol was determined at 22.2°. The average molecular weight of the upper layer obtained on mixing these liquids was found to be 52.5, which would give a percentage of carbon disulphide of 53 4. Interpolation from the data of Rothmund[3] would lead to 52.3. In cases of this kind, other analytical methods are sometimes troublesome.

Remarks on the Method.--The apparatus is considerably more compact than the Victor Meyer form, and stands at a convenient level above the working bench. It is very simply set up, requiring a single ring stand with two clamps, one of which holds the condenser.

If a constant be determined as suggested, correction is, of course, not necessary for the density of mercury or for its vapor pressure. If a record be kept of the volume of mercury employed, the constant need not be redetermined when the apparatus is next used.

---

[1] At normal pressure, chlorobenzene boils at 132°. The temperature of the jacket was 137 8°. As the pressure within the closed chamber increases, the volatilization of the chlorobenzene from the bulblet becomes rather slow.

[2] It will be seen that the values obtained for acetic acid, whose vapor is known to be associated, differ little from the monomolecular value. It must be recalled that, in this apparatus, the partial pressure of acetic acid vapor in the closed chamber is less than one-seventh of an atmosphere.

[3] *Z. physik. Chem.*, **26**, 475.

Correction for change of jacket temperature due to barometric change is negligible. Thus, 23 mm. change of barometer causes a change of 1° in the boiling point of toluene (384° absolute), or 1 part in 384 in the result.

When the final level of the mercury in the gage tube is very different from that measured in finding the constant of the apparatus, it is plain that the gas content of the test tube will be somewhat different. Correction for this is usually unnecessary, and was not made in the above examples.

As every portion of the enclosed chamber is kept at the constant high temperature, there is nothing to be feared from the diffusion of the vapor to colder parts of the apparatus, as in the case of the Lumsden or Victor Meyer apparatus. Thus, Lumsden remarks:[1] "The accuracy of the results depends very much on the rapidity with which the substance is vaporized, and this is the more important the smaller the molecular weight, since a vapor which diffuses rapidly may reach the colder part of the apparatus before a measurement of pressure can be made." Again, as no air is driven from a hotter to a colder place, no uncertain correction on this account has to be considered.[2]

Since the vapor is likely to be diffused throughout the whole of the test tube, and since the pressure read is less than one-sixth of an atmosphere, the partial pressure of the vapor cannot even locally much exceed one-sixth of an atmosphere. This low pressure lessens any tendency to association, as is seen in the acetic acid example given above. It is obvious that the test tube may be filled with an inert gas if desired.

Instead of a glass stopper, a one-holed rubber cork may be used at the lower temperatures. A glass rod, bent for the lowest centimeter of its length, passes through the hole, and by its timely rotation breaks the neck of the bulblet, which is inserted into a small blind hole beside it, and is pressed against the top of the gage tube. This form of "release" is perhaps easier to operate than that described above.

In the form described, this apparatus is not suitable for temperatures above 200°; but the examples given seem to show that it is both rapid and accurate for use at temperatures at which it is applicable.

RAPID DETERMINATIONS AND SEPARATIONS BY MEANS OF THE MERCURY CATHODE AND STATIONARY ANODE.

BY R. C. BENNER AND M. L. HARTMANN.

Received October 11, 1910.

The mercury cathode has been used for most metals which can be determined electrolytically. In the case of bismuth it is possible to make the determination with greater ease by this method than with platinum electrodes. The determination of chromium, while impossible by ordinary electrolytic methods, can be thus accomplished.

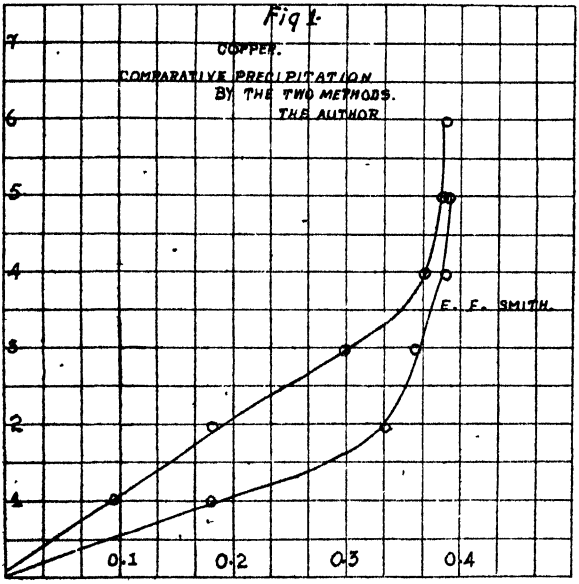
---

[1] *Loc. cit.*

[2] Cf. T. W. Richards, *Chem. News*, 59, 87.

The mercury cathode has been used with a stationary anode and low currents, as well as with the rotating anode and high currents, but not until recently has it been proven possible to use the stationary anode and high currents without some means of mechanical agitation.[1]

In order to determin what time could be saved by the use of the rotating anode, the rate of precipitation was determined without agitation under the same conditions as those used by Smith.[2] The curves in figures 1 and 2 show, that while the precipitation of copper and silver is more rapid when the rotating anode is used, the difference is not nearly as great as would be expected. This lack of rapidity is, moreover, much more than compensated for by the simplicity of the apparatus in case of the stationary anode.



It is possible to precipitate:

(1) 0.2075 gram of iron in 10 minutes with three to four amperes when the rotating anode is used.

(2) 0.1000 gram in the same time with four amperes when the solution is rotated by means of the solenoid.

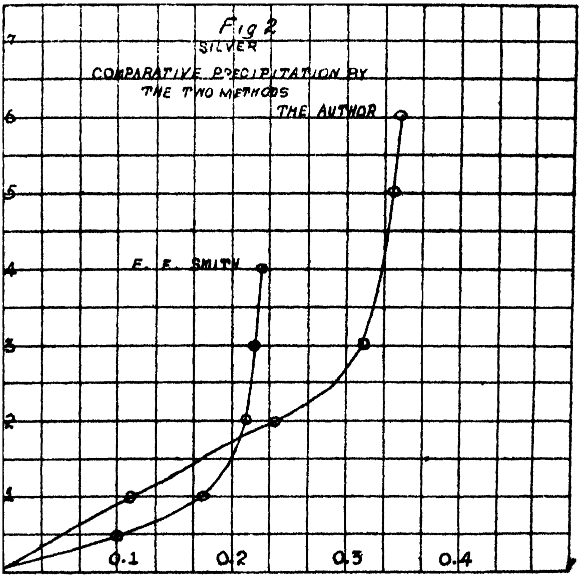
(3) 0.2007 gram in 20 minutes with the stationary anode and four

---

[1] Stoddard, This Journal, 31, 385; Benner, *Ibid.*, 32, 1231.

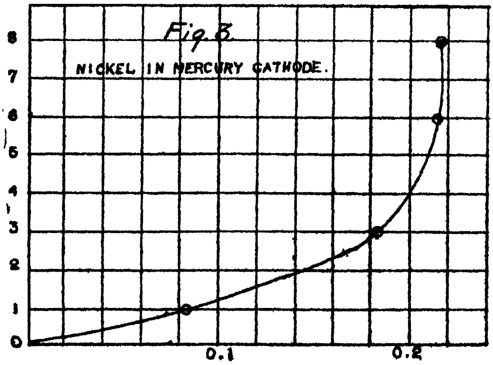
[2] "Electroanalysis," Phila., 1907.

amperes. Therefore, although there was no means at hand for making a direct comparison between this method and that in which the electrolyte was rotated by means of a solenoid,[1] it would seem that there is little, if anything, to be gained from magnetic rotation.



The following determinations and separations were carried out using the apparatus of our previous article.[2]

Nickel.—For the determination of nickel a solution of C. P. nickel sulphate was prepared and the nickel determined electrolytically.[3] It was found to contain 0.1089 gram of metallic nickel per 10 cc.:



---

[1] Frary, *Z. Elektrochem*, 1907, 308.

[2] THIS JOURNAL, 32, 1231.

[3] Smith, *Ibid.*, 25, 884.

Nickel taken.	Found	Error.	Amperes.	Volts.	Drops of acid.	Volume of solution.	Time.
0.1089	0.1096	+ 0.0007	3–4	7–8	8 H_2SO_4 1.84 sp. gr.	10	15
0.1089	0.1095	+ 0.0006	5–6	8–9	8 H_2SO_4	10	5
0.2178	0.2187	+ 0.0009	5–6	8–9	8 H_2SO_4	20	10
0.1089	0.1088	− 0.0001	5–6	8–9	2 H_2SO_4	10	10
0.1089	0.1084	− 0.0005	6–7	8–9	2 H_2SO_4	10	5
0.1089	0.1096	+ 0.0007	3–4	7–8	2 H_2SO_4 6 HNO_3	10	7
0.2178	0.2183	+ 0.0005	3–4	7–8	2 H_2SO_4 6 HNO_3	20	12
0.2178	0.2172	− 0.0006	3–4	7–8	2 H $_4$ 6 HNO_3	20	12
0.1089	0.1087	0.0002	4–5	9–10	5 HNO_3 2 H_2SO_4	10	10
0.1088	0.1086	− 0.0002	4–5	9–10	3 HNO_3 2 H_2SO_4	10	10
0.2178	0.2178	+ 0.0000	4–5	9–10	10 H_2SO_4	20	15
0.2178	0.2179	+ 0.0001	4–5	9–10	4 H_2SO_4	20	15
0.1089	0.1090	+ 0.0001	4–5	9–10	2 H_2SO_4	10	15
0.2178	0.2180	+ 0.0002	4–5	9–10	8 H_2SO_4	20	12

Rate of Precipitation of Nickel (Fig. 3).

0.2178	0.0859		5	13–14	2 H_2SO_4	20	1
0.2178	0.1858		5	13–14	2 H_2SO_4	20	3
0.2178	0.2125		5	13–14	2 H_2SO_4	20	5
0.2178	0.2146		5	13–14	2 H_2SO_4	20	6
0.2178	0.2182		5	13–14	2 H_2SO_4	20	8

SEPARATION OF NICKEL FROM ALUMINIUM.

Nickel taken.	Found.	Error.	Amperes	Volts.	Drops of acid.	Volume of solution.	Time.	Alumina.
0.1089	0.1088	− 0.0001	4–5	9–10	4 H_2SO_4	20	10	0.0904
0.1089	0.1087	− 0.0002	4–5	9–10	4 H_2SO_4	20	10	0.0904
0.1089	0.1083	− 0.0004	4–5	9–10	10 H_2SO_4	20	10	0.0904
0.1089	0.1083	− 0.0004	4–5	9–10	10 H_2SO_4	20	10	0.0904

SEPARATION OF NICKEL FROM TITANIUM

							Titanium dioxide
0.1089	0.1080	− 0.0009	4–5	9–10	10 H_2SO_4	20	0.0435
0.1089	0.1088	0.0001	4–5	9–10	10 H_2SO_4	20	0.0435

SEPARATION OF NICKEL FROM THE RARE EARTHS

							Oxide of the rare earths.
0.1089	0.1086	− 0.0003	4–5	9–10	2 H_2SO_4 3 HNO_3	20	0.2228
0.1089	0.1080	− 010009	4–5	9–10		20	0.2228

Reference to the table shows that with currents varying from three to six amperes, at seven to ten volts, it is possible to make accurate determinations of nickel, from a sulphate solution, either in the presence of from two to ten drops of sulphuric or four to six drops of nitric acid, when one or two drops of sulphuric acid are present, in 10 to 20 cc. of the electrolyte. The precipitation is sufficiently rapid for all practical purposes, as it is possible to precipitate 0.2178 gram of nickel from 20 cc. of solution in 8 minutes (Fig 3).

The determination of nickel in the presence of aluminium, titanium and the rare earths in a sulphuric acid solution, under the same conditions as were used for its determination alone, is as rapid and as accurate as when they are not present.

Cobalt.—A solution of cobalt sulphate was prepared from C. P. cobalt sulphate and made acid by the addition of a few drops of sulphuric acid. Ten cc. of the solution were found, by the electrolytic method,[1] to contain 0.1041 gram of metallic cobalt.

Cobalt taken.	Found	Error	Amperes.	Volts	Drops of acid. H_2SO_4	Volume.	Time.
0.1041	0.1037	— 0.0004	5-6	11-12	1	10	10
0.1041	0.1034	— 0.0007	5-6	11-12	1	10	10
0.2082	0.2090	+ 0.0008	3-4	6-7	1	20	20
0.1041	0.1044	+ 0.0003	3-4	6-7	1	20	20
0.1041	0.1042	+ 0.0001	3-4	6-7	1	10	8
0.1041	0.1041	+ 0.0000	4-5	7-8	1	10	10
0.1041	0.1036	— 0.0005	4-5	7-8	1	10	10
0.2082	0.2084	+ 0.0002	4-5	7-8	1	20	20
0.1041	0.1043	+ 0.0002	4-5	7-8	1	10	10
0.1041	0.1042	+ 0.0001	3-4	6-7	1	10	12
0.2082	0.2081	- 0.0001	3-4	6-7	1	20	..
0.2082	0.2085	+ 0.0003	3-4	6-7	1	20	.
Rate of Precipitation of Cobalt (Fig 4).							
0.3516	0.1885		5	6-7	1	20	3
0.3516	0.3039		5	6-7	1	20	6
0.3516	0.3428		5	6-7	1	20	9
0.3516	0.3510		5	6-7	1	20	12
0.3516	0.3512		5	6-7	1	20	15

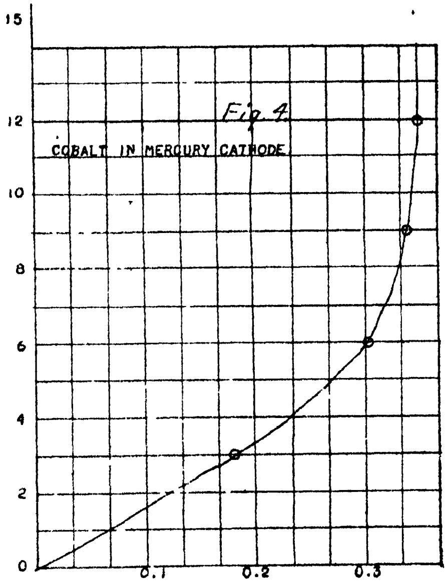
The determinations given in the table were carried out in solutions containing from 0.05 to 0.1 cc. of sulphuric acid and with currents varying from three to six amperes, at 6 to 12 volts. This gave complete precipitation of 0.1041 to 0.3516 of a gram of cobalt in from 10 to 15 minutes (Fig. 4). Results were good from weak sulphuric acid but not from strong acid solutions or those containing nitric acid.

Zinc.—A standard solution of zinc was prepared by dissolving a weighed amount of C. P. metallic zinc in sulphuric acid and diluting so that 10 cc. of the solution contained 0.2980 gram of metallic zinc and 0.3 cc. of sulphuric acid.

It was found that by carrying out the determination of zinc in a manner similar to the previous determinations of the other metals, it was possible to deposit zinc quantitatively either from solutions of the sulphate containing sulphuric acid or with nitric acid in the presence of a little sulphuric acid. The deposits were made with currents varying from three to six

---

[1] THIS JOURNAL, 25, 884.



amperes and at from four to seven volts, in 10 to 20 cc. of solution, with results equal to those obtained with low currents and the mercury cathode or with the rotating anode and mercury cathode:

Zinc taken.	Found.	Error.	Amperes.	Volts	Drops of acid.	Volume	Time.
0.2980	0.2978	− 0.0002	5–6	6–7	6 H_2SO_4	10	20
0.2980	0.2974	− 0.0006	5–6	6–7	6 H_2SO_4	10	20
0.2980	0.2975	− 0.0005	5–6	6–7	6 H_2SO_4	10	20
0.2980	0.2988	+ 0.0008	5–6	6–7	6 H_2SO_4 3 HNO_3	10	20
0.2980	0.2980	± 0.0000	5–6	6–7	6 H_2SO_4 3 HNO_3	10	20
0.2980	0.2988	+ 0.0008	4–5	6–7	6 H_2SO_4	10	20
0.5960	0.5966	+ 0.0006	4–5	6–7	9 H_2SO_4	20	25
0.5960	0.5964	+ 0.0004	3–4	6–7	9 H_2SO_4	20	25
0.5960	0.5963	+ 0.0003	5–6	6–7	9 H_2SO_4 3 HNO_3	20	25

Most of the determinations made with acid as strong as the following were low:

0.2980	0.2975	— 0.0005	7–8	4–5	12 H_2SO_4	10	15
0.2980	0.2975	— 0.0005	7–8	4–5	6 HNO_3 6 H_2SO_4	10	15

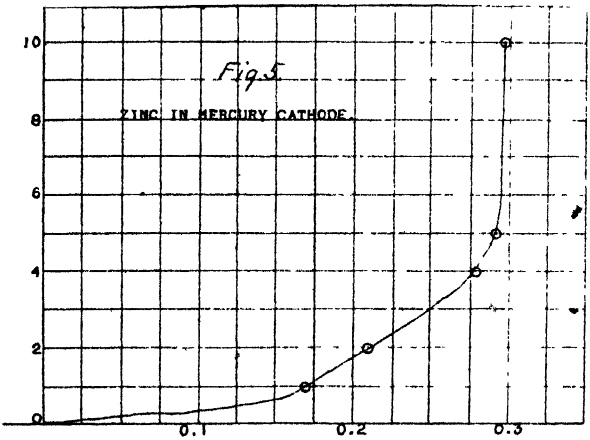
Rate of Precipitation of Zinc (Fig. 5).

0.2980	0.1690		4.5	5–6	6 H_2SO_4	10	1
0.2980	0.2097		4.5	5–6	6 H_2SO_4	10	2
0.2980	0.2458		4.5	5–6	6 H_2SO_4	10	3
0.2980	0.2843		4.5	5–6	6 H_2SO_4	10	4
0.2980	0.2976		4.5	5–6	6 H_2SO_4	10	5
0.2980	0.2985		4.5	5–6	6 H_2SO_4	10	10

SEPARATION OF ZINC FOR TITANIUM.

Taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.	Titanium dioxide.
0.2980	0.2975	— 0.0005	4–5	7–8	13	20	15	0.0435
0.2980	0.2989	+ 0.0009	4–5	7–8	13	20	15	0.0435
0.5960	0.5954	— 0.0006	3–4	7–8	13	20	25	0.0435
0.5960	0.5961	+ 0.0001	3–4	7–8	13	30	25	0.0435
0.2980	0.2989	+ 0.0009	3–4	7–8	13	20	15	0.0435
SEPARATION OF ZINC FROM ALUMINIUM.								
0.2980	0.2986	+ 0.0006	3–4	7–8	8	20	20	0.0904
0.2980	0.2990	+ 0.0010	3–4	7–8	8	20	20	0.0904
0.5960	0.5969	+ 0.0009	3–4	7–8	7	20	25	0.0452
0.5960	0.5965	+ 0.0005	3–4	7–8	7	20	25	0.0452

Using the same conditions as in the determination of zinc, it is possible to separate zinc from aluminium and titanium without difficulty.



Iron.—The standard solution of iron was made by dissolving a weighed amount of ferrous ammonium sulphate in water and making acid with sulphuric acid to prevent the formation of basic iron sulphate. Ten cc. of this solution contained 0.1002 gram of metallic iron and 0.11 cc. of sulphuric acid. Iron was determined with the usual apparatus by means of currents varying from 3–4 amperes at 7–8 volts. Solutions containing either nitric or sulphuric acid were used with very satisfactory results. The rate of precipitation with the mercury cathode is slower than that for most metals, it being possible to deposit in twenty minutes only 0.2004 gram of iron, from 20 cc. of solution, with a current of four amperes (Fig. 6).

The separation of iron from aluminium, titanium, the rare earths of the cerium and yttrium groups as extracted from monazite, was tried under the same conditions used for the determination of iron, with satisfactory results.

Iron taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.
0.1002	0.1003	+ 0.0001	3-4	7-8	6 H_2SO_4	20	10
0.1002	0.1000	— 0.0002	3-4	7-8	6 H_2SO_4	20	15
0.2004	0.2008	+ 0.0004	3-4	7-8	6 H_2SO_4	20	25
0.2004	0.2004	± 0.0000	3-4	7-8	6 H_2SO_4	20	25
0.2004	0.2002	- 0.0002	3-4	7-8	6 H_2SO_4	20	25
0.2004	0.2002	— 0.0002	3-4	7-8	2 H_2SO_4 4 HNO_3	20	25
0.1002	0.1003	+ 0.0001	3-4	7-8	2 H_2SO_4 4 HNO_3	20	15
0.2004	0.2000	— 0.0004	3-4	7-8	2 H_2SO_4 4 HNO_3	20	20
0.2004	0.2002	— 0.0002	3-4	7-8	2 H_2SO_4 4 HNO_3	20	25

Rate of Precipitation (Fig 6).

Iron taken.	Found.	Error.	Amperes.	Volts.	Drops of acid.	Volume.	Time.
0.2004	0.0302		4	7-9	6 H_2SO_4	20	1
0.2004	0.0795		4	7-9	6 H_2SO_4	20	2
0.2004	0.0998		4	7-9	6 H_2SO_4	20	3
0.2004	0.1522		4	7-9	6 H_2SO_4	20	5
0.2004	0.1918		4	7-9	6 H_2SO_4	20	10
0.2004	0.1957		4	7-9	6 H_2SO_4	20	15
0.2004	0.2007		4	7-9	6 H_2SO_4	20	20

SEPARATION OF IRON FROM ALUMINIUM.

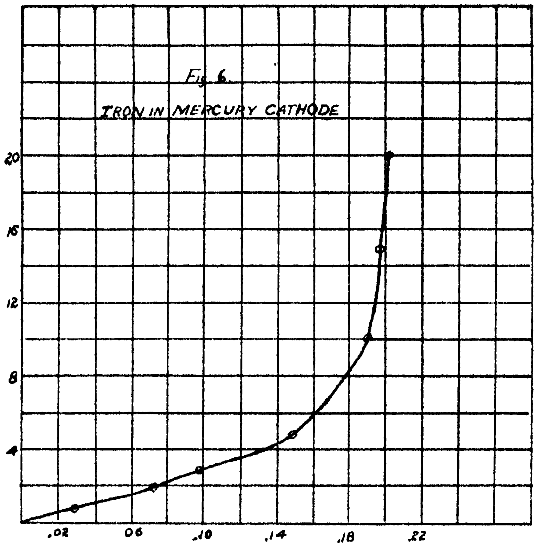
								Alumina.
0.1002	0.1005	+ 0.0003	4	7-9	8 H_2SO_4	20	15	0.0452
0.1002	0.1001	— 0.0001	4	7-9	8 H_2SO_4	20	15	0.0452
0.1002	0.1004	+ 0.0002	4	7-9	8 H_2SO_4	20	15	0.0452
0.1002	0.1000	— 0.0002	4	7-9	8 H_2SO_4	20	15	0.0452
0.1002	0.0995	- 0.0007	4	7-9	4 H_2SO_4 4½ HNO_3	20	15	0.0452
0.1002	0.1002	± 0.0000	4	7-9	4 H_2SO_4 4 HNO_3	20	15	0.0452
0.1002	0.1001	- 0.0001	4	7-9	4 H_2SO_4 4 HNO_3	20	15	0.0452

SEPARATION OF IRON FROM TITANIUM.

								Titanium dioxide.
0.1002	0.1000	— 0.0002	4	6-7	10 H_2SO_4	20	25	0.0435
0.1002	0.0994	— 0.0008	4	6-7	10 H_2SO_4	20	25	0.0435
0.1002	0.1002	± 0.0000	3-4	6-7	10 H_2SO_4	20	25	0.0435
0.1002	0.1000	— 0.0002	3-4	6-7	10 H_2SO_4	20	15	0.0435
0.1002	0.1009	+ 0.0007	3-4	6-7	10 H_2SO_4	20	15	0.0435
0.1002	0.1002	± 0.0000	3-4	6-7	10 H_2SO_4	20	15	0.0435

SEPARATION OF IRON FROM THE RARE EARTHS.

								Oxide of rare earths.
0.1002	0.1007	+ 0.0005	3-4	6-7	3 HNO_3 2 H_2SO_4	20	15	0.2228
0.1002	0.1003	+ 0.0001	3-4	6-7		20	15	0.2228



The exact variation of conditions can best be seen from the table given above.

Conclusion.

(1) Comparison of the rates of precipitation under like conditions of current, volume of solution, etc., shows that, although the rate of precipitation with the rotating anode is greater than with the stationary anode, it is not sufficiently so to recommend the use of so much more complex a piece of apparatus.

(2) The results obtained by this method are as accurate as those obtained by means of other mercury cathode methods.

(3) With the different metals determined it is possible to use about the same conditions as for the determination by means of the rotating anode and the mercury cathode.

University of Arizona, Tucson

CORRECTIONS.

"*A Simple System of Thermodynamic Chemistry Based upon a Modification of the Method of Carnot*" and "*The Fundamental Law for a General Theory of Solutions.*"—The two papers which appeared under the above titles in the April and May numbers of This Journal require the following corrections:

Page 479, line following equation (12), for V read *v*.

Page 486, equation 44, the term $(U + \Delta x RT)$ should be enclosed in parentheses.

Page 498 and page 666, the terms of the right-hand member of equation 85 should read *alternately plus and minus.*

Page 498, last line, page 654, first line, and page 667, second line, for *decrease* read *increase.*

Page 499, equation 86, the letter t has been omitted just in front of the last bracket sign.

In the 8th line of footnote 23 omit the negative sign before the last term of the equation.

Page 501, in equation 95 and the second line following it, for T read T_F.

Page 663, equation (111), for V read v.

Page 667, equation (126), for $\Delta C_{P_0} -$ read $\Delta C_{P_0} \Delta t_F +$. Equation (129) change the sign in front of each term containing α.

Page 670, line 20, for *to* read *by.*

Edward W. Washburn.

THE ELECTRON CONCEPTION OF VALENCE.

By K. George Falk and J. M. Nelson.

Received October 3, 1910

Introduction. 1. Limitations of the Problem. 2. Fundamental Hypothesis. 3. Carbon Compounds Containing Single Bonds. 4. Carbon Compounds Containing a Double Bond. 5. Carbon Compounds Containing a Triple Bond. 6. Relative Asymmetry. 7. Nitrogen Compounds Containing a Single Bond. 8. Nitrogen Compounds Containing a Double Bond. 9. Compounds Containing a Double Bond between Unlike Atoms. 10. Partial Valence. 11. Complex Inorganic Salts. 12. Summary.

Introduction.

In a paper published in 1909,[1] the hypothesis of Sir J. J. Thomson, according to which the linkages between atoms in a compound are caused by the transfer of corpuscles,[2] was applied to a number of facts drawn chiefly from organic chemistry. An attempt will be made in this paper to develop the subject somewhat farther. The same fundamental hypothesis, in the sense of a "supposition which it is expected will be useful" will be used. The deductions which will be made from this fundamental hypothesis are not put forward as the only explanation of the phenomena in question but as a possible explanation simpler in some ways in correlating facts than some of the explanations in current use, and in a few cases offering explanations for facts which have not been explained heretofore. The isomerism in compounds containing a double bond may serve to illustrate the former and the physical properties of the saturated dibasic acids the latter.

---

[1] *School of Mines Quarterly,* 30, 179.

[2] "The Corpuscular Theory of Matter," pp. 138–9 (1907).

1. Limitations of the Problem.

The valence of an element may be defined as a number which shows how many unit atoms or groups (with the hydrogen atom as unit standard) may be held in combination by an atom of that element. These valence numbers are purely the result of experimental investigations, but have been correlated to a great extent by the Periodic Law from which may now be taken the maximum valence of an element. The problem to be taken up here is limited by a clear conception of valence and the hypothesis to be used later. It may be stated, however, that stability relations of compounds, isomeric and otherwise, can enter only qualitatively in the discussion of valence since quantitative results can be arrived at by the use of the free energy relationships alone.

A valence theory, to be acceptable, must include or be able to account for all compounds known. The fact that the compounds predicted or suggested by the theory are not known would also be less disadvantageous for the theory than if compounds were known for which the theory was not able to account. This non-existence of compounds predicted by a theory may be due to the very limited range of conditions under which most of the substances known at present have been prepared.

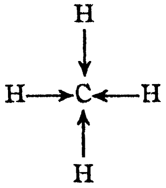
The subject of valence will not be taken up historically. Some or many of the ideas to be treated have been given before, but the work of those who have treated of this or of closely related subjects as for instance Abegg, and W. A. Noyes, will not be taken up in detail. It may be stated, however, that the scope of the subject matter and its treatment is different from that which has been given by others.

2. Fundamental Hypothesis.

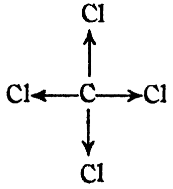
The hypothesis of Sir J. J. Thomson which will be elaborated here may be stated most concisely in his own words. "For each valency bond established between two atoms the transference of one (negatively charged) corpuscle from the one atom to the other has taken place, the atom receiving the corpuscle acquiring a unit charge of negative electricity, the other by the loss of a corpuscle acquiring a unit charge of positive. This electrical process may be represented by the producing of a unit tube of electric force between the two atoms, the tube starting from the positive and ending on the negative atom. . . . There is, however, one important difference between the lines representing the bonds and the tubes of electric force. The lines used by the chemist are not supposed to have direction. . . . On the electrical theory, however, the tubes of electric force are regarded as having direction starting from the positive and ending on the negative atom. . . . " This hypothesis supplements the structural formulas employed at present by giving the bonds direction. For convenience the lines which heretofore represented the bonds may be replaced by arrows, the direction of the arrows indicating the direction of the transfer of the corpuscles. Two atoms united in this way possess opposite electric charges. In regard to the direction of the valence when two atoms combine it seems fair to assume that this direction is ordinarily determined by the relative positions of the elements in the Periodic System. Namely, in the horizontal rows the elements of higher atomic weights are normally negative to the elements of smaller atomic weights. In the same vertical series, the main and subgroups must be considered separately, but on the whole the relations are fairly obvious here as well. This refers to the direction of the valences normally, but in certain cases the reverse direction may exist for a less stable form of a substance having the same composition. Thus, two forms of iodine chloride exist, which may be formulated $I \longrightarrow Cl$ and $I \longleftarrow Cl$, the presumption being that the former represents the stable form. Difficulty may also exist in assigning directed valences to compounds containing a number of linked carbon atoms, since the carbon atom appears to be able to take up a corpuscle or lose one with equal readiness. The inertness of carbon compounds in general also makes it more difficult to draw conclusions as to their structure and relative stabilities.

3. Carbon Compounds Containing Single Bonds.

In taking up the compounds of carbon containing single bonds, the introduction of directive valence will not be of much value since the chemistry of these compounds is worked out fairly completely and satisfactorily without it. It may be of interest, however, to call attention to some points. As examples, it may first be mentioned that, as J. J. Thomson points out,[1] methane and tetrachloromethane might be represented by the formulas:

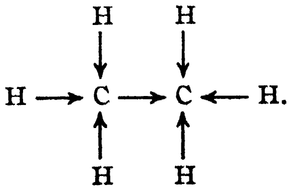


$$\begin{array}{c} H \\ \downarrow \\ H \rightarrow C \leftarrow H \\ \uparrow \\ H \end{array}$$



$$\begin{array}{c} Cl \\ \uparrow \\ Cl \leftarrow C \rightarrow Cl \\ \downarrow \\ Cl \end{array}$$

The carbon atom in methane has gained four corpuscles, while that in tetrachloromethane has lost four. Ethane is represented by the formula



$$\begin{array}{ccccccc} & & H & & H & & \\ & & \downarrow & & \downarrow & & \\ H & \rightarrow & C & \rightarrow & C & \leftarrow & H. \\ & & \uparrow & & \uparrow & & \\ & & H & & H & & \end{array}$$

---

[1] *Loc. cit.*, p. 131.

In ethane, therefore, one of the carbon atoms will have a charge of four units of negative electricity and the other of two units, or comparing the carbon atoms of the two methyl groups, one will be negatively charged, the other positively. With ethane there is no evidence as to whether such a condition exists, but it may apply in the case of hexaphenyl ethane. Thus if Gomberg's triphenyl methyl is assumed to be hexaphenyl ethane, then the two triphenylmethyl groups composing it would be charged differently, and it is an interesting fact that solutions of the substance conduct the electric current[1] and that Gomberg early in his investigations explained this by assuming the existence of the "pseudoions" $(C_6H_5)_3C^+$ and $(C_6H_5)_3C^-$.

In the solid state, then, hexaphenylethane, colorless, would be present; in solution, the colored ions exist, and are more reactive than the unionized organic compound, as is generally the case. The same is true of the triphenylmethyl halides. The application of this view to the substances related to triphenylmethyl recently described by Schlenk[2] is obvious.

The saturated dicarboxylic acids may also be taken up briefly. In malonic acid the arrangement of the groups may be represented by $(CO_2H) \longleftarrow CH_2 \longrightarrow (CO_2H)$, the molecule being symmetrical. In succinic acid, the arrangement would be $(CO_2HCH_2) \longrightarrow (CH_2CO_2H)$,—unsymmetrical; in glutaric acid, $(CO_2HCH_2) \longleftarrow CH_2 \longrightarrow (CH_2CO_2H)$,—symmetrical; in adipic acid, $(CO_2HCH_2CH_2) \longrightarrow (CH_2CH_2CO_2H)$, or unsymmetrical; in pimelic acid, symmetrical again, and so on. These acids would therefore fall into two groups—those with an even number of carbon atoms having unsymmetrical directive valences, and those with an odd number of carbon atoms having symmetrical directive valences, and the acids of each group would be strictly homologous only with the acids of the same group. The fact that the saturated dibasic acids differ in properties depending upon whether an even or an odd number of carbon atoms is present is a well-known one and is spoken of in all text-books of organic chemistry. Thus the acids containing an even number of carbon atoms have higher melting points and smaller solubility than the acids with an odd number of carbon atoms immediately preceding and succeeding them, but show regularities when compared with the next acids with an even number of carbon atoms. These relations are accounted for when directive valences are considered. It is probable that similar relations apply to the saturated monobasic acids, but the direction of the valences cannot be shown as yet with sufficient certainty in their cases.

---

[1] *Ber.*, 35, 2397; Walden, *Z. physik. Chem.*, 43, 451.

[2] *Ann.*, 372, 1.

4. Carbon Compounds Containing a Double Bond.

In taking up compounds of carbon containing a double bond, it is not possible to make any simple assumption regarding the direction of the valence when two groups combine, as was done with the singly bonded substances. It is necessary to consider all the possible cases and from a study of the reactions decide which formula may be assigned to a given compound.

The compounds containing a double bond may in general be divided into two classes: (1) compounds in which the two halves of the molecule are similar; and (2) compounds in which the two halves of the molecule are dissimilar. To the first class belong the substances of the general types $CR_2 : CR_2$ and $CRR' : CRR'$. Introducing the conception of directive valence, it is evident that there are possibilities of the existence of two isomers in each case; that is, the two valences (or corpuscles) may proceed from one carbon atom to the other, or one may proceed in one direction and one in the other;[1] or formulated as follows: $CR_2 \rightleftarrows CR_2$ and $CR_2 \rightrightarrows CR_2$; $CRR' \rightleftarrows CRR'$ and $CRR' \rightrightarrows CRR'$. If two isomers exist in any case, one would be expected to be more stable than the other; if only one substance of the general type exists, then it may be that the other is too unstable to be formed permanently, going over into the stable form, and it would be a question then, to determin by means of the chemical reactions of the substance, to which of the two types its reactions show it to conform best.

Of substances derived from the type $CR_2 : CR_2$ none is known to exist in two forms.

Thörner and Zincke[2] observed the formation of a hydrocarbon melting at 243–4°, on heating α-benzopinacolin with soda lime at a temperature of 350–80°. They thought, from its composition, that it might be identical with tetraphenylethylene, even though it showed a higher melting point. On account of these observations of Thorner and Zincke it seemed worth while to test the possible existence of more than one form of tetraphenylethylene But in no case have the results confirmed this supposition.

Some of the methods tried to bring about the transformation of tetraphenylethylene consisted in heating the alcoholic solution of the substance with both alkali and acids, and with rapid and slow cooling of the solution for the subsequent crystallization and also cystallizing in the dark as well as in the direct sunlight. In place of acids or alkali, iodine was used in a similar way, but tetraphenylethylene was again obtained having the original melting point. Next tetraphenylethylene was heated above its melting point and then suddenly chilled and it was also distilled and the distillate suddenly cooled, but no change was observed.

---

[1] In those cases where one valence proceeds in one direction and one in the other it is assumed that the corpuscles which are transferred are localized on the atoms, as otherwise the carbon atoms would become electrically neutral, but no assumption is made as to their relative positions except for the one case where four unlike atoms or groups are combined, when the phenomena of optical activity demonstrate that the four directions of valences do not lie in one plane. This localization is tacitly assumed in all cases.

[2] *Ber.*, 11, 1396 (1878).

Tetraphenylethylene was also prepared by different methods, such as heating dichlorodiphenylmethane with diphenylmethane in a sealed tube for two days at 300°. Tetraphenylethylene was obtained in this way, but with much greater difficulty than where the two halogens are on different carbon atoms, as in case of mono-homo-diphenyl methane which yielded tetraphenylethylene very easily and is the method generally employed for its preparation. Tetraphenylethylene was also obtained in small amounts by heating benzophenone and diphenylmethane in the presence of phosphorus pentoxide. In both of the above methods, however, the melting point of the tetraphenylethylene was 220°. As a conclusion from these experiments it seems highly improbable that there exists an isomeric tetraphenylethylene.

The direction of the valences in the compounds of this group might be determined by following some of the addition reactions of closely related compounds. Since the molecule is perfectly symmetrical, it makes no difference in the resulting compound, in which way another substance, HI for instance, is added. If, however, as a typical example, propylene $CH_3.CH:CH_2$ is taken, there would be three possibilities: $MeCH \rightleftarrows CH_2$ and $MeCH \rightrightarrows CH_2$ or $MeCH \leftleftarrows CH_2$. On treating with HI, if either of the last two represents the structural formula, the I would all go to one carbon atom, and the H to the other, only one substance being formed; while if the first represents the structure, a mixture of two substances should be formed, the H and I being divided between the two carbon atoms. The reactions in this case might be represented as follows:

$$MeCH \underset{H \longrightarrow I}{\rightleftarrows} CH_2 = MeCH_2 \longrightarrow CH_2I \text{ and } MeCH \overset{I \longleftarrow H}{\rightleftarrows} CH_2 = MeCHI \longleftarrow CH_3.$$

The extent to which each of the products would be formed would depend upon the influence of the methyl group as compared with the hydrogen or the double bond, and upon the difference in polarity between the hydrogen and iodine; the smaller the difference the more nearly equal would be the amounts of the two products formed.

The following results were obtained by A. Michael:[1]

Propylene + HI formed principally $(CH_3)_2CHI$ together with a little $C_2H_5CH_2I$.

Propylene + ClBr yielded 5 parts $CH_3.CHBr.CH_2Cl$ to 7 parts $CH_3.CHCl.CH_2Br$.

Propylene + ClI yielded 1 part $CH_3.CHI.CH_2Cl$ to 4 parts $CH_2.CHCl.CH_2I$.

Propylene + HOCl formed principally $CH_3.CHOH.CH_2Cl$ and perhaps a little $CH_3.CHCl.CH_2OH$.

These examples have been quoted in order to throw some light, if possible, upon the direction of the valences in unsaturated compounds existing in one form, and they indicate that this form has the structure $CR_2 \rightleftarrows CR_2$. Propylene does not belong to this type of compound; but it seems fair to carry over the conclusions arrived at with propylene to the symmetrical compounds and to assign this structure to the substance, if only one form exists, and if two forms exist, to assign it to the more stable of the two.

---

[1] *J. prakt. Chem.*, 60, 286–384, 409–86 (1899).

Of substances derived from the type $CRR':CRR'$ a large number of isomers are known, of which maleic and fumaric acids may serve as examples. The two forms of this type using the directive valences are $CRR' \rightleftarrows CRR'$ and $CRR' \rightrightarrows CRR'$ of which the former represents the more stable, the latter the less stable form. These two groups of substances belong to the fumaroid and maleinoid types, the fumaroid being the more stable, showing the higher melting point, less solubility and volatility, smaller heats of combustion, less color (if any is shown by either isomer), and, in the case of acids, smaller ionization constants than the maleinoid, all these properties being only different expressions for the difference in stability between the two forms. It will hardly be necessary to enter into a detailed description of the different substances included in this class. The possibilities of addition would be worked out in each case by the method indicated with propylene.

With the substances containing a double bond in which the two halves of the molecule are dissimilar, there are a greater number of possibilities, namely, $CR_2:CRR'$; $CR_2:CR'_2$; $CR_2:CR'R''$; $CRR':CR'R''$; $CRR':CR''R'''$. In each of these cases, using directive valences, there would be three isomers possible, one valence acting in each direction, both valences acting in one direction, and both in the opposite direction. The three possible isomers corresponding to these are not known for any one substance with certainty. The reason for this may be found in the fact that if the two halves of the molecule are made up of groups differing very much in properties, of the two isomers in which both valences act in the same direction, one will exhibit very much greater stability than the other, making it extremely difficult, if not impossible, to isolate the less stable form.

With regard to the cinnamic acids, it appears advisable at present to delay the application of directive valences until the properties of the isomers have been studied sufficiently in the solid and liquid states as well as in solution to allow of more definit characterization of each form than is possible at present.

The reaction described by Michael and Bunge,[1] according to which both the fumaroid and maleinoid crotonic acids add chlorine either in sunlight or the dark to form the same maleinoid dichloride can readily be accounted for with directive valences.

[1] *Ber.*, 41, 2907 (1908).

The application to benzene and some of its derivatives is obvious, but will not be enlarged upon here.[1]

Note added November 12.—Stobbe and Wilson[2] prepared three forms of the para- and of the meta-nitrobenzaldeoxybenzoin and showed that they are true isomeric chemical compounds. The existence of the three forms can be accounted for with directive valences as described, but the structure to be assigned to each form is as yet uncertain.

5. Carbon Compounds Containing a Triple Bond.

With regard to carbon compounds containing a triple bond, there are evidently many possibilities in the way of drawing formulas involving directive valences, most of which are entirely unnecessary, if not actually incapable of realization, at the present time, since very few, if any, isomeric compounds of this kind are known. It may be shown, however, that the stable form of triple-bonded compounds is in all probability best represented by the structure $RC \underset{\longleftarrow}{\overset{\longrightarrow}{\longrightarrow}} CR'$. Taking acetylene dicarboxylic acid, perhaps the simplest example which could be chosen, treatment with 10 per cent. hydrobromic acid at ordinary temperatures for five days yielded bromofumaric acid, the conditions being such that bromomaleic acid would not be transformed into bromofumaric acid.[3] The same was found in the case when hydrochloric acid was used. The reaction here is

$$(CO_2H)C \underset{\longleftarrow}{\overset{\longrightarrow}{\longrightarrow}} C(CO_2H) + HBr = (CO_2H)BrC \underset{\longleftarrow}{\longrightarrow} CH(CO_2H).$$

Bromine and acetylenedicarboxylic acid yielded 30 per cent. dibromomaleic acid and 70 per cent. dibromofumaric acid. Considering the structure of acetylenedicarboxylic acid,

$$(CO_2H)C \underset{\longleftarrow}{\overset{\longrightarrow}{\longrightarrow}} C(CO_2H),$$

and the reagent bromine, it is evident that there is the same chance or tendency of addition to each of the three bonds, or that one-third of the compound would be transformed into

$$(CO_2H)BrC \underset{\longrightarrow}{\longrightarrow} CBr(CO_2H)$$

and two-thirds into $(CO_2H)BrC \underset{\longleftarrow}{\longrightarrow} CBr(CO_2H)$.

6. Relative Asymmetry.

The introduction of directive valence into organic formulas does not affect the view of the tetrahedral form of the carbon atom in so far as this applies to single bonds. This view only requires that the four valences do not act in one plane.[4] The case is different, however, for the double-bond isomerism. Without going into the advantages and disadvantages of the theory of "geometrical isomerism," it may be pointed out that directive valences afford an explanation for the existence of isomers which does not involve the spatial relations between the groups at all but refers the isomerism to the double linkage between the atoms.

---

[1] This has been done in the preliminary paper, pp. 187–8.

[2] *Ann.*, **374**, 237 (1910).

[3] Michael, *J. prakt. Chem.*, [2] **46**, 210 (1892).

[4] It may be pointed out that the existence of the third active malic acid (Crassulaceen-malic acid) may be explained by the direction of the valence between the central carbon atoms (for the properties of this acid cf. Werner, *Lehrbuch der Stereochemie*, p. 114).

The subject of relative asymmetry which appears to involve both the tetrahedral model and geometrical isomerism remains to be considered.

Without entering into the details of the question, it may be stated that if "pseudoasymmetry" be extended to those cyclic compounds for which the explanation of relative asymmetry has been used, the experimental facts will permit of explanation without involving the position of the groups on one side or the other of the ring.[1] This has been pointed out by A. W. Stewart in his book on "Stereochemistry"[2] in which he states that "relative asymmetry" is only a special case of "pseudoasymmetry."

7. Nitrogen Compounds Containing a Single Bond.

The study of the compounds of nitrogen in which directive valence (or transfer of corpuscles) takes the place of the usual method of linkage between the atoms may be pursued in the same way as with the compounds of carbon. The nitrogen atom has the power of taking up three corpuscles, as shown by ammonia, or of losing five. The latter cannot be seen directly since the compounds of nitrogen with the univalent elements capable of taking up corpuscles (namely, the halogens) are unstable under ordinary conditions, but is evident from the compounds of nitrogen with oxygen. The difference between the two extreme states of nitrogen would be eight units of valence, or the nitrogen in ammonia differs from the nitrogen in nitric acid by eight corpuscles. The difference in the direction of the valence (or the loss or gain of corpuscles) can be followed much more readily with the nitrogen than with the carbon compounds, since a more evident difference in the properties of the compounds results, making it fairly easy to follow a given nitrogen atom containing a certain charge through a series of compounds and their derivatives. Nitrogen in addition to being able to take up three corpuscles is able to take up a fourth, if at the same time one is also given up, ammonium compounds being formed.[3] With the compounds of nitrogen, just as with carbon, if an element or group is joined by means of a single bond, this bond may be assumed to have a definit direction depending upon whether the element or group is electronegative (capable of taking up a corpuscle) or electropositive (capable of giving up a corpuscle) toward the nitrogen. A possible exception to this may be quoted from an article by Meisenheimer,[1] in which he considered it probable that in methylethylphenylhydroxyl ammonium hydroxide, the two hydroxyl groups are united to the nitrogen by unequal valences.

---

[1] For the development of "pseudoasymmetry" cf. Werner, *Loc. cit.*, pp. 29 and 129.

[2] P. 142.

[3] Cf. Sir William Ramsay, *J. Chem. Soc.*, 93, 785 (1908).

In hydrazine, using directive valences, the two nitrogen atoms should have different properties ($H_2 \rightrightarrows \underset{(\alpha)}{N} \longrightarrow \underset{(\beta)}{N} \leftleftarrows H_2$), the α atom possessing one negative charge, the β atom three negative charges. If a compound containing two molecules of hydrochloric acid and one of hydrazine is formed in which both nitrogen atoms are pentavalent, then the β nitrogen atom having gained four corpuscles and lost one is comparable to the nitrogen atom in ammonium salts and the α nitrogen atom having gained three corpuscles and lost two is comparable to the nitrogen atom in amine oxides or amine dihalides. The properties of hydrazine dihydrochloride bear out this comparison. Of the two hydrochloric acid molecules which may be added, one is given off readily, and hydrazine itself behaves more like a substance capable of forming a mono-acid base than a di-acid base. Substituting the hydrogen atoms of hydrazine by different groups, in general only one compound would be stable even if an isomer should be formed under exceptional circumstances (for instance $RHN \longrightarrow NHR'$ and $RHN \longleftarrow NHR'$). If the entering groups do not differ from each other too greatly, it would be possible to isolate such unstable isomers in some cases. This appears to have been done by Willgerodt[2] by the reaction between dinitrochlorobenzene and phenylhydrazine or α- or β-naphthylhydrazine, and perhaps in other cases.

8. Nitrogen Compounds Containing a Double Bond.

The compounds of nitrogen containing a double bond would include the azo and diazo derivatives. It will not be necessary to go into detail with the azo compounds, since so few isomers belonging to this class are known.[3]

Among the diazo compounds it will be necessary to include the diazonium compounds, which will be spoken of first. These are derived from ammonium salts in which the three hydrogen atoms are replaced by one nitrogen atom which shows similar properties. The formula of the diazonium salts may therefore be represented by

$$R \longrightarrow \underset{\substack{\downarrow \\ X}}{N} \Lleftarrow N,$$

one nitrogen being the ammonia nitrogen combined with RX, the other being the nitrous acid nitrogen. For the syn and anti diazo compounds there are evidently the two formulas containing the groupings $.\mathrm{N} \leftleftarrows \mathrm{N}.$ and $.\mathrm{N} \leftrightarrows \mathrm{N}.$ possible. In the formation of diazo compounds from a primary amine and nitrous acid, the first product formed is always the syn compound making it extremely probable that these are derived from the grouping $\mathrm{R.N} \leftleftarrows \mathrm{N.X}$ or $\mathrm{R} \longrightarrow \mathrm{N} \leftleftarrows \mathrm{N} \longrightarrow \mathrm{O} \longleftarrow \mathrm{H}$, the ammonia and nitrous acid nitrogens retaining their charges. Syn compounds can very readily be converted into anti compounds, most simply by the action of alkali in solution, but anti compounds cannot be converted directly again into syn, showing that the anti form is the more stable. This is also brought out by comparing some of the physical properties[1] of the two series. The anti diazo compounds may then be assigned the structure $\mathrm{R} \longrightarrow \mathrm{N} \rightleftarrows \mathrm{N} \longrightarrow \mathrm{O} \longleftarrow \mathrm{H}$ analogous to the stable forms of the ethylene isomers in which the two valences also act in opposite directions. The chemical reactions which show the syn compounds to be more reactive than the anti are their greater explosiveness and the fact that they can be more easily reduced and oxidized. In coupling, the syn compounds also show their great reactivity as compared with the anti.

---

[1] *Ber.*, 41, 3966 (1908).

[2] *J. prakt. Chem.*, [2] 37, 449 (1888); 43, 177 (1891).

[3] The only certain cases of isomerism here appear to be with *p*-azophenol, Willstätter and Benz, *Ber.*, 39, 3492 (1906); 40, 1578 (1907) and with azobenzene, Gortner and Gortner, THIS JOURNAL, 32, 1294 (1910).

The relation between syn diazo compounds and diazonium compounds is a very close one. They are readily transformed into each other, alkalies favoring the formation of the diazo derivatives, acids of the diazonium, while in solution both exist in equilibrium testifying to the readiness with which they are transformed into each other. All this is readily understood when directive valences are used, the structure of the two classes being represented by

$$\mathrm{R} \longrightarrow \mathrm{N} \leftleftarrows \mathrm{N} \longrightarrow \mathrm{X} \text{ and } \begin{array}{l} \mathrm{R} \longrightarrow \mathrm{N} \overset{\leftarrow}{\leftleftarrows} \mathrm{N}, \\ \phantom{\mathrm{R} \longrightarrow{}} \downarrow \\ \phantom{\mathrm{R} \longrightarrow{}} \mathrm{X} \end{array}$$

the X group or element (electronegative toward nitrogen as the direction of the valence shows) shifting its bond from the one nitrogen to the other.

The replacement of the diazo group by other groups on the benzene (or naphthalene) nucleus is a well-known and characteristic property of these compounds. The more unstable syn derivatives decompose in this way fairly readily, the ease, of course, depending to some extent upon the substance used, while with the anti derivatives these reactions do not occur, or are very slow in their progress. The greater reactivity of the syn compounds would perhaps account for this, but it seems possible in this case to look for a deeper underlying cause. The great variety of groups which combine with the benzene nucleus when the nitrogen is eliminated, including hydroxyl, alkoxyl, halogen, cyanogen, sulphur, sulphonic acid, aromatic hydrocarbon residues, etc., shows that the reaction is not limited to any one group or class. The common phenomenon in all these reactions is the elimination of nitrogen and the cause of the reaction may justly therefore be found in the tendency of the nitrogen to be set free. The difference in the nitrogen in the syn and anti diazo compounds may be represented by $\longrightarrow \mathrm{N} \substack{\longleftarrow \\ \longleftarrow} \mathrm{N} \longrightarrow$ and $\longrightarrow \mathrm{N} \substack{\longleftarrow \\ \longrightarrow} \mathrm{N} \longrightarrow$ and upon being set free, if the trivalent nitrogen still persists, the syn would be represented by $\mathrm{N} \substack{\longleftarrow \\ \longleftarrow \\ \longleftarrow} \mathrm{N}$ and the anti by $\mathrm{N} \substack{\longleftarrow \\ \longleftarrow \\ \longrightarrow} \mathrm{N}$. If the trivalent property becomes transformed into some other, then there appears to be no reason why one form should give off the nitrogen any more readily than the other. The reaction is then referred back to the tendency of the nitrogen in the diazo compounds to form the nitrogen molecule $\mathrm{N} \substack{\longleftarrow \\ \longleftarrow \\ \longleftarrow} \mathrm{N}$. This leads to the conclusion that in the nitrogen molecule, the two atoms are charged differently, one positively, the other negatively. The same fact is indicated by the formation of nitrogen when ammonium nitrite is heated, and the reverse action.[1]

---

[1] The syn compounds are more soluble and show a lower melting point than the anti.

9. Compounds Containing a Double Bond between Unlike Atoms.

So far isomerism caused by two atoms of an element combined in different ways, which was explained as being due to the difference in the direction of the valence, has been considered chiefly. The same principles should be applicable to combinations of different elements and the possibilities of isomerism due to the double bond in these cases should follow analogous rules. Following the reasoning used in the example already discussed, it is possible to limit the cases of possible isomerism somewhat in considering combinations of two dissimilar elements. When two dissimilar elements unite by a single bond, the direction in which the corpuscle is moved in order to establish this linkage is, in general, perfectly definit, the opposite direction occurring only under exceptional conditions. If a second linkage (or a double bond) is established between the two atoms, the direction in which the second corpuscle moves will either be the same or opposite to that of the first corpuscle, giving rise to two isomeric compounds of the same structure differing only in the direction of one valence. These two isomers would differ in stability, and the more stable one may for the present be assigned the structure in which both valences possess the same direction, since this appears to be the most reasonable view in the union of two dissimilar atoms. This subject may be exemplified by the carbonyl group. Following the reasoning given, the structure $:C \rightrightarrows O$ would be the stable one; if an isomer occur, the grouping $:C \rightleftarrows O$ would be assigned to it, whereas the grouping $:C \leftleftarrows O$ would be so unstable as to render the compounds in which it might be expected to exist, too unstable to be isolated. These stable isomers differ in structure then from the stable isomers in which two carbon or nitrogen atoms are united by a double bond, the direction of the two valences being opposite to each other in the latter, in the same direction in the former.

---

[1] This deduction holds only for the nitrogen molecule, but the conclusion that an atom may possess a different charge depending upon the conditions is not new. Cf. W. A. Noyes, *J. Am. Chem. Soc.*, 32, 1070. " . . . . This is in accord with the hypothesis first proposed by the writer in 1901 (*Ibid.*, 23, 463) that atoms of the same element may in different cases assume either positive or negative charges. Essentially the same fundamental idea has been proposed quite independently by Abegg and, from a wholly different point of view, by J. J. Thomson."

A large number of isomeric compounds containing a double bond between two unlike atoms are known. To begin with the simplest case of all, benzophenone is known to exist in two modifications, one stable, the other labile and going over into the stable form with great ease. Of these modifications, the stable one, melting at 48.5°, may be assigned the structure $(C_6H_5)_2C \rightrightarrows O$ and the labile one, melting at 25°, the structure $(C_6H_5)_2C \rightleftarrows O$.[1] Other ketones which exist in two modifications are known. Among these may be mentioned *p*-tolylphenylketone, stable variety melting at 59–60°, labile variety melting at 55°, and fluorenone. Perhaps the two forms of *o*-quinone and of diphenoquinone belong to this group.

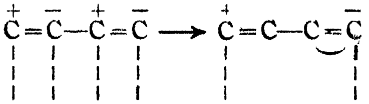
A group of substances derived from the ketones, or in general from compounds containing the carbonyl group, occur in isomeric forms which may be explained in the same way as with the simple ketones. The classes showing this isomerism are the oximes, hydrazones, semicarbazones, chloroimides, etc. It seems hardly necessary to enter into any details with regard to the structures of these classes of compounds, since the method of treatment is the same as that already used, and the stability and other relations would be taken up similarly. A few lines may, however, be devoted to the oximes. On treating an aromatic aldehyde with hydroxylamine directly the "anti" aldoxime is formed first and can be converted into the "syn" form by suitable treatment. From this, the anti form would be assigned the structure $RH : C \rightrightarrows N \longrightarrow O \longleftarrow H$ and the syn form the structure $RH : C \rightleftarrows N \longrightarrow O \longleftarrow H$. The different properties of the two forms of the aldoxime would then be due to the difference in linking between the carbon and nitrogen atoms in the two cases. Similar reasoning applies to the ketoximes, the structure to be assigned to the two forms which differ in the union between the carbon and nitrogen atoms and the reactions of these forms differing according to the influence of that union. In the Beckmann rearrangement, the group which would exchange positions with the hydroxyl depends upon the nature of that group as compared with the nature of the nitrogen atom.

[1] Schaum, *Chem.-Ztg.*, 47, 417 (1910) states that the two modifications differ chemically.

Thus the isomerism which has been explained heretofore by geometrical isomerism in all these classes may be referred to the direction of the two valences in the double bond without considering the spatial position of the groups. All double-bond isomerism may be attributed to the same cause.

10. Partial Valence.

The fundamental hypothesis used in this paper to account for chemical combination requires that the atoms joined by the transfer of a corpuscle should possess electric charges, the atom which loses the corpuscles, a positive charge, the atom which gains the corpuscle, a negative. In general, therefore, the parts of a molecule should be charged differently, and should therefore be able to attract the parts of other molecules possessing opposite charges. This attraction evidently will be different in character and intensity from the attraction between two atoms combined chemically by the transfer of a corpuscle. In this connection it is of interest to quote from Thiele's original paper on partial valence in which the analogy between double bonds and molecular magnets is drawn, in which he does not, however, refer the forces to the action of electric charges:[1] "Man könnte sich einen solchen Ausgleich vielleicht so vorstellen, dass the Atome einer Doppelbindung entgegengesetzt positiv und negativ geladen seien, $\overset{+}{C} = \overset{-}{C}$. Bei benachbarten Doppelbindungen würden sich dann the inneren Ladungen ausgleichen:



.

Man erhielte dann eine Anordrung, ähnlich der, die benutzt wurde, im mit Hülfe der 'Molekularmagnete' die Constitution der Magnete zu erklären."

Evidently with the use of directive valence, the charges on the atoms are not distributed as simply as pictured in this analogy, but each atom or group combined with the carbon atoms involved will have its effect on these. It would also not be necessary for each of the carbon atoms involved to exert its attractive force. It may be pointed out that the partial valences need not be, and probably are not, the most important factors involved in causing a chemical reaction to take place, and that all that need be assumed is that they exert a directive influence on the entering groups or atoms when addition takes place to a double bond. This fact harmonizes the conclusions drawn so far in this section with those obtained in the sections where the direction of the valences in double bonds were considered. Explanations for individual reactions on the basis of this view, which accounts for partial valence as the attraction of the electrically charged parts of a molecule will not be given here.

---

[1] *Ann.*, 306, 89–90 (1899).

Within recent years, partial valence has been used to explain a somewhat different phenomenon, namely, the formation of quinhydrones,[1] while "Nebenvalenzen" have been used to account for the existence of a number of isomeric compounds by Hantzsch.[2] With the view of partial valence, which may include the "Nebenvalenzen" as used by Hantzsch, developed here it would then appear that the electric attraction between certain atoms or groups of the same or different molecules is sufficiently strong to produce configurations stable enough to exist under ordinary conditions and to produce characteristic individual effects, such as in the first case mentioned, distinctive color. The laws governing these differences in intensity of the partial valences can only be found as a result of experimental investigation.

Electric attraction between electrically charged atoms has suggested a possible explanation for an entirely different class of phenomena, namely, that of the anomalies existing in aqueous solutions of highly ionized electrolytes. The following quotations are taken from a paper by A. A. Noyes.[3] ". . This principle is that the ionization of salts, strong acids, and bases is a phenomena primarily determined not by specific chemical affinities, but by electrical forces arising from the charges on the ions. . . . . . "

"The molecular explanation of these facts and the more general conclusions drawn from them would seem to be that primarily the ions are united somewhat loosely in virtue of their electrical attraction to form molecules, the constituents of which still retain their electric charges and therefore to a great extent, their characteristic power of producing optical effects and such other effects as are not dependent on their existence as separate aggregates. Secondly, the ions may unite in a more intimate way to form ordinary uncharged molecules, whose constituents have completely lost their identity and original characteristics. These two kinds of molecules may be designated electrical molecules and chemical molecules, respectively, in correspondence with the character of the forces which are assumed to give rise to them. . . . The facts, moreover, indicate that chemical molecules are formed from the ions in accordance with the principle of mass-action, but that electrical molecules are formed in accordance with an entirely distinct principle, whose theoretical basis is not understood."

It is evident that the two kinds of molecules referred to here are strictly comparable with the substances spoken of as formed by the transfer of corpuscles (chemical bonds) and those formed by electrical attraction or partial valence, with the addition that in aqueous solution phenomena are made apparent and predominate which do not appear to an appreciable extent with the organic compounds which were chiefly considered heretofore.

---

[1] Willstätter, *Ber.*, 1908, and others.

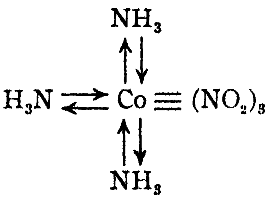
[2] Hantzsch, *Ber.*, 1910, chiefly.

[3] THIS JOURNAL, 30, 351–2 (1908).

11. Complex Inorganic Salts.

The direction of the valence in the simple inorganic salts which ionize in aqueous solution can readily be determined. Some interesting conclusions have been pointed out for these in the section on Partial Valence. The complex inorganic salts cannot be treated in as simple a manner. It is not necessary, however, to develop the hypothesis for these here as this has already been done by Sir William Ramsay in his Presidential Address before the London Chemical Society in 1908.[1] The part of this address relating to the subject in question will be quoted and may serve to show how the assumptions made may be applied to the cobaltammine nitrites:.[2]

"Just as the nitrogen atom in NH_4Cl takes one electron from the hydrogen of the HCl and gives one up to the chlorine, so it appears reasonable to suppose that in these cobaltammines each nitrogen atom of the three ammonia groups takes from the cobalt atom one electron, while it gives one at the same time. The formula of the triammino-nitrite would therefore be



$$\begin{array}{ccc} & NH_3 & \\ & \uparrow\downarrow & \\ H_3N \rightleftarrows & Co & \equiv (NO_2)_3 \\ & \uparrow\downarrow & \\ & NH_3 & \end{array}$$

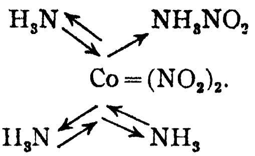
If another molecule of ammonia be added, then the cobalt atom gives to the nitrogen of the ammonia an electron, but does not receive one in return. The nitrogen atom of that ammonia group is then "overloaded" for it has received four electrons in addition to its normal five,[3] making nine in all; now it appears that no element can be associated with more than eight in all. Hence that nitrogen atom must lose an electron. This it imparts to one of the (NO_2) groups, which parts company with the cobalt atom, and, as a complex ammonium nitrite is now present, it is ionizable on solution in water. A glance at the proposed formula will explain the conception

---

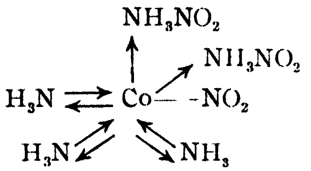
[1] "The Electron as an Element," *J. Chem. Soc.*, 93, 774.

[2] Pp. 785–7.

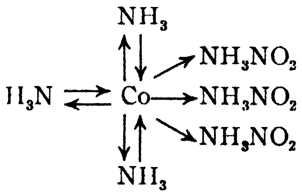
[3] The nitrogen atom is assumed by Ramsay to carry five corpuscles normally. In the deductions given here this assumption is not made in the same form, but practically the same assumption, based also upon experimental facts, is made with regard to the number of corpuscles which an atom is able to gain or lose.



The remaining formulas[1] may be written similarly, thus:



and



Why is the group $Co(NH_3)_3(NO_2)_3$ not ionizable? Let us first inquire: Why is cobalt nitrate ionizable? (Cobalt nitrite is unknown). Because the cobalt atom gives up an electron to each of the three NO_3 groups, remaining itself an ion. That is, the metal cobalt has three electrons associated with it; what we call "metallic cobalt" is a "tri-electride of cobalt." As "cobaltion," it has parted with its three electrons. But in the last of the compounds above, the cobalt has not three electrons at its disposal; it has already parted with them to the NH_3NO_2-groups. And we are led to conclude that in the non-ionizable compound the cobalt does not, as in its ordinary salts, part with three electrons, but that it receives them from the nitro groups."

This explanation of the cobaltammine nitrites evidently agrees with the views of structure developed here. The nomenclature differs slightly from that in general use. The formulation of other complex salts could doubtless be carried out in the same way, but will not be attempted here as it is only desired to show the possibilities of the conception of directive valences.

12. Summary.

An attempt has been made in this paper to apply the hypothesis of J. J. Thomson, according to which chemical bonds are formed by the transfer of a corpuscle from one atom to another, to a number of classes of compounds.[2]

The most interesting result obtained is that all cases of isomerism connected with the presence of a double bond, whether between like or unlike atoms, have been referred to the direction of the valences of the double bond, instead of to spatial configurations as heretofore.

The existence of certain isomers and the explanation of some hitherto unexplained reactions have also been referred to the directions of the valences.

---

[1] For the remaining cobaltammine nitrites.

[2] This is not the only hypothesis which may be used. The interesting deductions of J. Stark (*Jahrb. der Rad. Elekt.*, 5, 124 (1908)) based upon a different fundamental assumption may be cited, although he includes chiefly phenomena of a different kind.

The existence of "partial valence" is shown to follow from the electric charges of the atoms in a molecule.

Applications of the hypothesis to inorganic compounds have been taken from the work of A. A. Noyes and of Sir William Ramsay.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, BOSTON,
COLUMBIA UNIVERSITY, NEW YORK.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. No. 183.]

RESEARCHES ON QUINAZOLINES (TWENTY-SIXTH PAPER). THE SYNTHESIS OF SOME STILBAZOLES, HYDRAZONES AND SCHIFF BASES IN THE 4-QUINAZOLONE GROUP.[1]

BY MARSTON TAYLOR BOGERT, GEORGE DENTON BEAL AND CARL GUSTAVE AMEND.

Received September 24, 1910.

Various papers from this laboratory[2] have shown that in the 4-quinazolone group it is a relatively simple matter to prepare derivatives carrying a methyl group in position 2 and amino groups on either or both the benzene and miazine portions of the nucleus. Such substances constitute interesting material for the study of the action of these various groups with aldehydes.

For, it is well known that methyl groups on a nuclear carbon adjacent to the nitrogen of a heterocycle, as, for example, in the α-picolines, the quinaldines, and the like, easily condense with aldehydes to compounds of the type R.CH : CH.R′, in which R represents the heterocycle and R′ the radical of the aldehyde used.[3] For compounds of this type where R′ is a simple or substituted benzene nucleus, the name "stilbazole" has been introduced,[4] on account of the structural similarity of such substances to the stilbenes.

The condensation of aldehydes with *Bz*-amino compounds, or anilines, to compounds of the R.N:CH.R′, or Schiff base type, is also an old story.

Bülow[5] and others[6] have shown that aldehydes condense to hydrazones with the *N*-amino groups of nitrogen heterocycles.

---

[1] Read at San Francisco meeting of the Society, July 15, 1910.

[2] Bogert *et al*, THIS JOURNAL, 32, 784 and 1297 (1910).

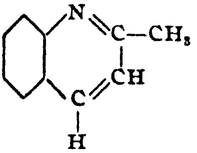
[3] Jacobsen and Reimer, *Ber.*, 16, 2006 (1883); Wallach and Wusten, *Ibid.*, 16, 2008 (1883); Döbner and Miller, *Ibid.*, 18, 1646 (1885); Ladenburg, *Ibid.*, 19, 439 (1886); Baurath, *Ibid.*, 20, 2719 (1887), and 21, 818 (1888); Bulach, *Ibid*, 20, 2047 (1887); Heyman and Königs, *Ibid.*, 21, 1424 and 2167 (1888); Eckhardt, *Ibid.*, 22, 279 (1889); Busch and Königs, *Ibid.*, 23, 2682 (1890); von Grabski, *Ibid.*, 35, 1956 (1902); Löw, *Ibid.*, 36, 1666 (1903); and others.

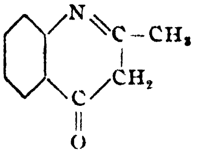
[4] Baurath, *Loc. cit.*

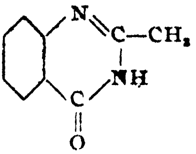
[5] *Ber.*, 40, 4749 (1907).

[6] Bogert and Gortner, THIS JOURNAL, 31, 947 (1909).

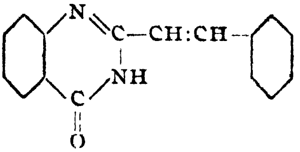
The first 4-quinazolone studied by us was the 2-methyl-4-quinazolone, whose structure resembles that of quinaldine or, still more closely, that of γ-quinaldone,


Quinaldine.


γ-Quinaldone.


2-Methyl-4-quinazolone.

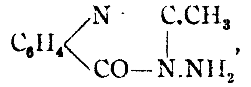
It condenses easily with aromatic aldehydes to the stilbazole; with benzaldehyde, for example, giving the simple styryl derivative,



Boiling with caustic alkali, or with strong hydrochloric acid, fails to hydrolyze these compounds to aldehyde and quinazolone again. By virtue of the $-\mathrm{CO.NH}- \rightleftarrows -\mathrm{C(OH)} : \mathrm{N} \longrightarrow$ grouping in the quinazoline portion of the molecule, they dissolve in caustic alkalies and are reprecipitated from such solutions by carbon dioxide or by weak organic acids.

2,3-Dimethyl-4-quinazolone gives the corresponding 2-styryl-3-methyl-4-quinazolone with benzaldehyde. As the condensation product in this case cannot assume the enolic condition, it is insoluble in caustic alkali solutions.

Passing on to the 2-methyl-3-amino-4-quinazolone,



$$C_6H_4\left\langle\begin{array}{l}N\cdot\ \ C.CH_3\\ \qquad\quad |\\ CO-N.NH_2\end{array}\right.,$$

the opportunity was presented for the aldehyde to condense with either the 2-methyl or the 3-amino group, giving in the one case a stilbazole (*C*-benzal), in the other a hydrazone (*N*-benzal), or, finally, with excess of aldehyde, condensation might be effected with both groups simultaneously, yielding a compound which would be both stilbazole and hydrazone in structure. As will be seen from the experiments described beyond, representatives of all three of these classes have been obtained. In connection with these experiments, the following observations are of interest:

1. With benzaldehyde and the quinazolone in equimolecular proportion, the condensation occurs first with the *N*-amino group, giving the hydrazone.

2. With excess of aldehyde, the dimolecular condensation follows, *i. e.*, aldehyde condenses with both the methyl and the amino group.

3. The hydrazone is readily hydrolyzed by boiling dilute hydrochloric acid, while the stilbazole is unaffected by this treatment. Hence, on boiling the dimolecular condensation product with 10 per cent. hydrochloric acid, the stilbazole, 2-styryl-3-amino-4-quinazolone, which could not be prepared by direct condensation, was easily obtained.

4. With cinnamic aldehyde, salicylic aldehyde, or vanillin, the aldehyde condenses only with the *N*-amino group. Heating either these hydrazones or the original 2-methyl-3-amino-4-quinazolone with excess of the aldehyde does not give the di-aldehyde condensation product, although, as has been mentioned already, these aldehydes condense freely with the 2-methyl in the absence of the 3-amino group. But, if these hydrazones be heated with benzaldehyde, then the 2-methyl is immediately changed to the styryl group. From which, it might be inferred either that this 2-methyl group is much more reactive towards benzaldehyde than towards the other aromatic aldehydes mentioned, or that if the failure of the other aldehydes to give di-aldehyde condensations is due to steric hindrance, the presence of another aldehyde group in position 3 does not prevent the entrance of the benzal group in position 2.

2-Methyl-7-amino-4-quinazolone presents a slightly different condition of affairs. Like the 2-methyl-3-amino-4-quinazolone, condensations are possible here with the methyl, the amino group, or with both. The amino group is, however, differently located in the molecule, being on the benzene and not on the miazine side of the nucleus, and in union with carbon instead of with nitrogen. Aldehydes condensing with this amino group should thus yield true Schiff bases instead of hydrazones.

In our first experiment with the 2-methyl-7-amino-4-quinazolone and benzaldehyde, a mono-benzal derivative was obtained which was apparently the Schiff base, since it could be hydrolyzed into aldehyde and quinazolone again by long boiling with dilute potassium hydroxide solution. Subsequent attempts to get this same product all failed. Irrespective of the amount of benzaldehyde used with the quinazolone, the same product resulted in all other experiments, but a product different from the one obtained in the first experiment. The fact that this product obtained in most of the experiments can be acetylated would argue the presence therein of an unchanged amino group. We do not feel satisfied with the results with this particular quinazolone, and if an opportunity presents will repeat the work. It is contrary to our experience in other cases that the 7-amino group should condense more readily with benzaldehyde than the 2-methyl, and the mono-benzal derivative isolated in the first experiment must be obtained again and further studied before we are convinced that in it the benzaldehyde has condensed with the 7-amino group.

No such complications appeared in the interaction of 2-methyl-7-

acetamino-4-quinazolone and benzaldehyde, which resulted in a smooth condensation between the aldehyde and the 2-methyl group.

In the case of 2,3-dimethyl-7-amino-4-quinazolone also, the mono-benzal condensation product obtained proved to be the styryl compound, *i. e.*, the stilbazole, from which it can be gathered that, under the conditions of our experiment at least, the 2-methyl reacts with benzaldehyde more rapidly than the 7-amino group.

Finally, in the 2 methyl-3,7-diamino-4-quinazolone, we find three groups capable of taking part in the reaction with aromatic aldehydes, yielding respectively stilbazoles, hydrazones, or Schiff bases, or compounds containing two or all of these functions simultaneously.

On heating this quinazolone with excess of benzaldehyde, all three groups reacted, the tri-benzal derivative being the chief product. At the same time there were formed two isomeric di-benzal derivatives, but in amount insufficient to identify.

When the 7-amino group was acetylated, the 2-methyl and 3-amino groups condensed smoothly with the benzaldehyde. The 6-acetamino isomer behaved similarly. When both 3- and 7-amino groups were acetylated, the 2-methyl group could be similarly condensed with the aldehyde.

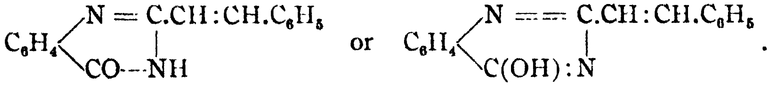
Summing up, then, our results would seem to show that, with reference to their activity towards benzaldehyde, and under the conditions of our experiments, the above groups can be arranged in the following order: first, the 3-(or *N*-) amino group; second, the 2-methyl group; and third, the 7-(or *Bz*-) amino group.

Experimental.

I. Condensations with 2-Methyl-4-quinazolone.

With the exception of the first, compounds carrying the —CO.NH— $\rightleftarrows$ —C(OH) : N— group are written in the keto form and called quinazolones.

2-Styryl-4-quinazolone (2-Styryl-4-hydroxyquinazoline),



$$C_6H_4\left\langle\begin{array}{l} N = C.CH:CH.C_6H_5 \\ \qquad\quad | \\ CO\!-\!NH \end{array}\right. \quad \text{or} \quad C_6H_4\left\langle\begin{array}{l} N == C.CH:CH.C_6H_5 \\ \qquad\qquad | \\ C(OH):N \end{array}\right. .$$

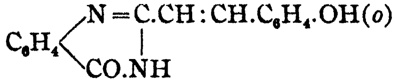
2-Methyl-4-quinazolone was mixed with slightly more than the equimolecular amount of benzaldehyde and the mixture boiled for ten minutes over the naked flame. The melt, crystallized from alcohol, yielded colorless, silky needles, melting at 252–3° (cor.).

Found: N, 11.86. Calculated for $C_{16}H_{12}ON_2$: N, 12.0.

The compound is rather difficultly soluble in alcohol, chloroform or glacial acetic acid; very difficultly soluble in ether or carbon disulphide. The benzal group is not broken off by boiling with potassium hydroxide solution or with hydrochloric acid. With bromine, in chloroform or glacial acetic acid solution, it yields a mono-bromo substitution product. No di-bromo addition was noted.[1] An effort was made to oxidize the styryl quinazolone to the 4-quinazolone-2-carboxylic acid by the method of Bamberger and Berle,[2] but the results were unsatisfactory.

In an attempt to get the intermediate alkine (*i. e.*, $C_9H_6ON_2.CH_2.CH(OH).C_6H_5$), equimolecular amounts of 2-methyl-4-quinazolone and benzaldehyde, mixed with some water, were heated in a sealed tube for 40 hours at 140°. At the close of the heating the tube was found to be filled with crystals, which when recrystallized from alcohol proved to be identical with the above 2-styryl-4-quinazolone.

2-o-Hydroxystyryl-4-quinazolone,



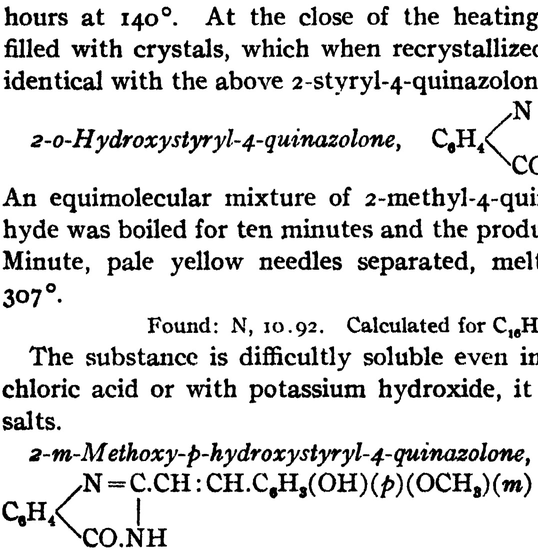
$$C_6H_4\left\langle\begin{array}{l} N = C.CH:CH.C_6H_4.OH(o) \\ \quad\;\; | \\ CO.NH \end{array}\right.$$

. — An equimolecular mixture of 2-methyl-4-quinazolone and salicylic aldehyde was boiled for ten minutes and the product crystallized from alcohol. Minute, pale yellow needles separated, melting with decomposition at 307°.

Found: N, 10.92. Calculated for $C_{16}H_{12}O_2N_2$: N, 10.60.

The substance is difficultly soluble even in hot alcohol. With hydrochloric acid or with potassium hydroxide, it yields bright canary-yellow salts.

2-m-Methoxy-p-hydroxystyryl-4-quinazolone,



$$C_6H_4\left\langle\begin{array}{l} N = C.CH:CH.C_6H_3(OH)(p)(OCH_3)(m) \\ \quad\;\; | \\ CO.NH \end{array}\right.$$

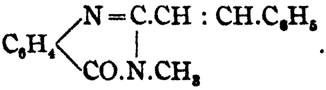
.—Equimolecular amounts of 2-methyl-4-quinazolone and vanillin were fused together over the flame until crackling ceased (ten minutes). The cold melt was crystallized repeatedly from alcohol. Pale yellow, minute needles resulted, which softened at about 275° (cor.) and at 280° (cor.) melted down to a brownish liquid.

Found: N, 9.63. Calculated for $C_{17}H_{14}O_3N_2$: N, 9.52.

The alkaline salts are a darker yellow, but possess no tinctorial power.

II. Condensation with 2,3-Dimethyl-4-quinazolone.

2-Styryl-3-methyl-4-quinazolone,



$$C_6H_4\left\langle\begin{array}{l} N = C.CH : CH.C_6H_5 \\ \quad\;\; | \\ CO.N.CH_3 \end{array}\right.$$

. — 2,3-Dimethyl-4-quinazolone and benzaldehyde were boiled together until the crackling ceased, and the cold melt was then crystallized from dilute alcohol. Fine, light yellow needles were obtained, melting at 170° (cor.).

Found: N, 10.72. Calculated for $C_{17}H_{14}ON_2$: N, 10.68.

To make certain that the 2-methyl group was the only one participating in the above reaction, some 3-methyl-4-quinazolone was heated with benzaldehyde for 6–8 hours at 180°, but no condensation ensued.

---

[1] Compare Wallach and Wusten, *Ber.*, 16, 2009 (1883); Dubke, *Ibid.*, 27, 79 (1894).

[2] *Ann.*, 273, 330.

III. Condensation with 2-Methyl-3-amino-4-quinazolone.

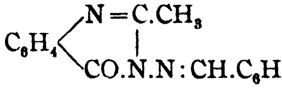
The 2-methyl-3-amino-4-quinazolone was prepared by the method of Bogert and Gortner,[1] from acetoanthranil and hydrazine hydrate.

In one case, however, another product was isolated, which we believe to be

Acetoanthranilic acetohydrazide, $CH_3CONH.C_6H_4.CONHNHCOCH_3$.—Acetoanthranil was stirred into an excess of aqueous hydrazine hydrate solution and the mixture warmed until complete solution resulted. Alcohol was then added and on dilution with water a white precipitate separated, melting at 180°, and thought at first to be impure acetoanthranilic acid (m. p. 186°). It was therefore boiled with acetic anhydride, to regenerate the acetoanthranil, but on cooling a product was obtained which crystallized from alcohol or from acetic anhydride in prisms, melting at 193° (cor.).

Found: N, 17.98. Calculated for $C_{11}H_{13}O_3N_3$: N, 17.94.

2-Methyl-3-benzalamino-4-quinazolone,



$$C_6H_4\left\langle\begin{array}{l}N=C.CH_3\\ \quad |\\ CO.N.N:CH.C_6H_5\end{array}\right.$$

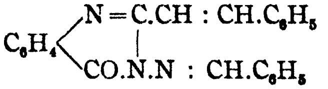
.—This has already been described by Bogert and Gortner,[2] who prepared it by boiling together for a few minutes 2-methyl-3-amino-4-quinazolone and benzaldehyde. It forms colorless prismatic needles. They give its melting point as 183° (cor.). By careful purification, we have succeeded in raising this to 187° (cor.). The condensation may be accomplished by boiling together the two constituents dry or, still better, by boiling them together in alcoholic solution.

Further heating with benzaldehyde, converts this mono-benzal derivative into the di-benzal compound described beyond.

Hydrochloride.—The powdered base was suspended in dry ether and a stream of dry hydrogen chloride passed in. When the reaction was complete, the precipitate was filtered out, washed with dry ether, and dried in vacuum over solid potassium hydroxide and concentrated sulphuric acid. It was then a nearly colorless amorphous powder, softening at 220° and decomposing without melting at about 300°.

Found: N, 14.15; Cl, 11.53. Calculated for $C_{16}H_{13}ON_3.HCl$: N, 14.01; Cl, 11.85.

2-Styryl-3-benzalamino-4-quinazolone,



$$C_6H_4\left\langle\begin{array}{l}N=C.CH:CH.C_6H_5\\ \quad |\\ CO.N.N:CH.C_6H_5\end{array}\right.$$

.—2-Methyl-3-amino-4-quinazolone and benzaldehyde were mixed, in the proportion of one molecule of the former to two of the latter, and the mixture boiled for five or ten minutes. The solution was allowed to cool somewhat and was then poured into ten volumes of hot alcohol. On cooling, yellow crystals separated, which were purified by recrystallization from alcohol and then appeared in minute, nearly colorless stellate tufts, melting at 155° (cor.).

---

[1] This Journal, 31, 947 (1909).

[2] *Loc. cit.*

Found: N, 12.04. Calculated for $C_{23}H_{17}ON_3$: N, 11.96.

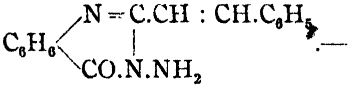
The benzal group attached to the nitrogen is easily broken out of this compound by hydrolysis with dilute mineral acid or with caustic alkali, while that attached to the CH is unaffected by such treatment. Even on boiling in simple alcoholic solution, the benzalamino group seems to suffer partial or slow hydrolytic cleavage, for the odor of benzaldehyde soon becomes quite pronounced in the recrystallization of the compound.

The same substance was obtained by heating either 2 styryl-3-amino-4-quinazolone or 2-methyl-3-benzalamino-4-quinazolone with benzaldehyde.

Hydrochloride.—Some of this was separated in the hydrolysis of the above substance with hydrochloric acid. It is a yellowish solid, not melting below 300°.

Found: N 10.52. Calculated for $C_{23}H_{17}ON_3$ HCl: N, 10.83.

2-Styryl-3-amino-4-quinazolone,



$$C_6H_6\left\langle\begin{matrix}N=C.CH:CH.C_6H_5\\ \quad|\\ CO.N.NH_2\end{matrix}\right.$$

.—2-Styryl-3-benzalamino-4-quinazolone was stirred into an excess of boiling dilute (10 per cent.) hydrochloric acid, and the benzaldehyde formed driven out with steam. The resultant clear solution was precipitated with sodium hydroxide and the yellow resinous precipitate purified by repeated crystallization from alcohol. Snowy plates, or broad needles, were thus obtained, melting at 164° (cor.).

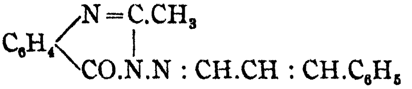
Found: N, 16.03. Calculated for $C_{16}H_{13}ON_3$: N, 15.97.

Heated with benzaldehyde, the 2-styryl-3-benzalamino-4-quinazolone is reproduced.

2-Styryl-3-benzoylamino-4-quinazolone.—The above quinazolone was suspended in water and treated with benzoyl chloride and a little caustic alkali. The crude product crystallized from alcohol in colorless needles, melting at 195° (cor.).

Found: N, 11.59. Calculated for $C_{23}H_{17}O_2N_3$: N, 11.44.

2-Methyl-3-cinnamalamino-4-quinazolone,

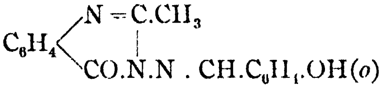


$$C_6H_4\left\langle\begin{matrix}N=C.CH_3\\ \quad|\\ CO.N.N:CH.CH:CH.C_6H_5\end{matrix}\right.$$

.—An equimolecular mixture of 2-methyl-3-amino-4-quinazolone and cinnamic aldehyde was boiled for ten minutes. The crude product was crystallized from alcohol, treated with boneblack in alcoholic solution, and finally recrystallized from dilute alcohol. It then appeared in broad, bright yellow needles, melting at 148–9° (cor.).

Found: N, 14.23. Calculated for $C_{18}H_{15}ON_3$: N, 14.53.

2-Methyl-3-salicalamino-4-quinazolone,



$$C_6H_4\left\langle\begin{array}{l} N=C.CH_3 \\ \quad | \\ CO.N.N\ .\ CH.C_6H_4.OH(o) \end{array}\right. .$$

—A mixture of 2-methyl-3-amino-4-quinazolone and salicylic aldehyde, in the proportion of one molecule of the former to two of the latter, was boiled ten minutes, the solution cooled somewhat, and poured into five times its volume of hot alcohol. On cooling, short, pale yellow needles separated, melting at 171° (cor.).

Found: N, 14.91. Calculated for $C_{16}H_{13}O_2N_3$: N, 14.53

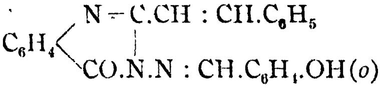
On hydrolysis with hydrochloric acid or with potassium hydroxide solution, salicylic aldehyde is split out. Long boiling with excess of salicylic aldehyde fails to introduce another aldehyde group. It does not yield an acetamino derivative with acetic anhydride.

Potassium Salt.—Bright yellow.

Hydrochloride.—The quinazolone was suspended in dry ether and dry hydrogen chloride passed in The hydrochloride is a bulky yellowish powder, melting with decomposition at about 250°.

Found N, 13.50 Calculated for $C_{16}H_{13}O_2N_3.HCl$ N, 13.31

2-Styryl-3-salicalamino-4-quinazolone,

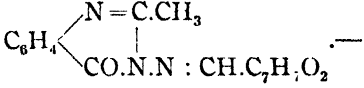


$$C_6H_4\left\langle\begin{array}{l} N=C.CH:CH.C_6H_5 \\ \quad | \\ CO.N.N:CH.C_6H_4.OH(o) \end{array}\right. .$$

—While the 2-methyl-3-salicalamino-4-quinazolone refused to condense with another molecule of salicylic aldehyde, it did condense with benzaldehyde when the two were boiled together for about ten minutes. The product crystallized from alcohol in yellowish needles, melting at 232–3° (cor.).

Found: N, 11.60. Calculated for $C_{23}H_{17}O_2N_3$: N, 11.44

2-Methyl-3-vanillalamino-4-quinazolone,



$$C_6H_4\left\langle\begin{array}{l} N=C.CH_3 \\ \quad | \\ CO.N.N:CH.C_7H_7O_2 \end{array}\right. .—$$

2-Methyl-3-amino-4-quinazolone was fused with twice the calculated amount of vanillin until water ceased to be evolved. On cooling, a pale yellow solid was obtained. This was pulverized and crystallized twice from alcohol, giving small yellowish prisms, or minute needles, melting at 215–6° (cor.).

Found: N, 13.77. Calculated for $C_{17}H_{15}O_3N_3$ N, 13.59.

With hydrochloric acid, or with potassium hydroxide, it forms deep yellow salts which show no tinctorial power.[1] Boiled with hydrochloric acid, the odor of vanillin appears.

---

[1] Compare *Ber.*, 39, 2749 (1906).

IV. Condensations with 2-Methyl-7-amino-4-quinazolone.

2-Methyl-7-amino-4-quinazolone and Benzaldehyde.—In the first experiment, the aminoquinazolone was boiled for ten minutes with excess of benzaldehyde. The clear solution on cooling deposited rosettes of needles, which on recrystallization from alcohol appeared in short, silky needles of a pale cream color, melting at 324° (cor.).

Found: N, 16.1. Calculated for $C_{16}H_{13}ON_3$: N, 15.97.

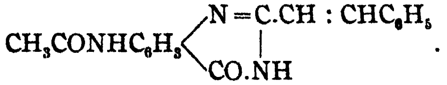
It is readily soluble in nitrobenzene, amyl alcohol or acetone; moderately soluble in boiling alcohol; difficultly soluble or insoluble in ether, chloroform, carbon tetrachloride or benzene. With concentrated hydrochloric acid, it turns a deep orange-yellow. Long boiling with dilute (10 per cent.) potassium hydroxide solution very slowly splits it into the aldehyde and quinazolone again.

Attempts to get this product a second time invariably failed. In all cases, apparently irrespective of the amount of benzaldehyde used, the product after careful purification by repeated crystallization from alcohol, melted at 324–5°. A mixture of this substance with that obtained in the first experiment showed a depression of 17° in the melting point and the analytical figures do not check either with those calculated for a mono- or a di-benzal derivative:

Found: C, 68.77 and 68.89; H, 5.38 and 4.91; N, 13.88, 13.94 and 13.72. Calculated for a mono-benzal derivative ($C_{16}H_{13}ON_3$): N, 15.97; for a di-benzal derivative ($C_{23}H_{17}ON_3$): N, 11.97.

The substance is not appreciably soluble in ether, chloroform, carbon tetrachloride or benzene. It dissolves in acetone, ethyl or amyl alcohol, or in nitrobenzene. With concentrated hydrochloric acid, it turns first yellow and then the color is discharged. With acetic anhydride, it gives an acetyl derivative which crystallizes from alcohol in colorless pearly plates, melting at 274–6° (cor.) and containing 12.57 per cent. of nitrogen.

2-Styryl-7-acetamino-4-quinazolone,



$$CH_3CONHC_6H_3\left\langle\begin{array}{l}N=C.CH:CHC_6H_5\\ \quad\;\;|\\ CO.NH\end{array}\right.$$

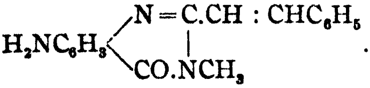
. — 2-Methyl-7-acetamino-4-quinazolone was boiled with benzaldehyde and the solid product crystallized from alcohol. Short, colorless needles, melting at 323–4° (cor.).

Found: N, 13.65 and 13.94. Calculated for $C_{18}H_{15}O_2N_3$: N, 13.77.

The compound is not appreciably soluble in water or ether, but dissolves readily in acetone, ethyl or amyl alcohol, or in nitrobenzene. Treated with concentrated hydrochloric acid, it first turns intensely yellow, then the color is largely discharged. On boiling, it dissolves slowly in the acid.

V. Condensations with 2,3-Dimethyl-7-amino-4-quinazolone.

2-Styryl-3-methyl-7-amino-4-quinazolone,



$$H_2NC_6H_3\left\langle\begin{array}{l}N=C.CH:CHC_6H_5\\ \quad|\\ CO.NCH_3\end{array}\right.$$

.—As before, the aminoquinazolone was merely boiled with benzaldehyde. On cooling, the crude product separated in yellow nodules, which were removed, washed with cold alcohol and then dissolved in hot alcohol. Water was added carefully to the hot alcoholic solution, and as the solution cooled yellow, twinned prisms crystallized out. On recrystallization, these melted at 229.5–230° (cor.). The mother liquor from these crystals showed a faint greenish fluorescence.

Found: N, 15.31. Calculated for $C_{17}H_{15}ON_3$: N, 15.16.

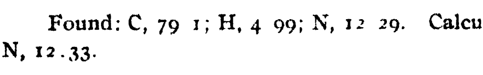
Heated with acetic anhydride, it yields the monoacetyl derivative described below.

2-Styryl-3-methyl-7-acetamino-4-quinazolone was prepared by boiling the above amino compound with acetic anhydride, as just stated, or by condensing the 2,3-dimethyl-7-acetamino-4-quinazolone with benzaldehyde. Purified by repeated crystallization from alcohol, it forms yellowish needles, melting at 272° (cor.).

Found: N, 13.32. Calculated for $C_{19}H_{17}O_2N_3$: N, 13 17.

VI. Condensations with 2-Methyl-3,7-diamino-4-quinazolone.

2-Styryl-3,7-dibenzalamino-4-quinazolone,



$$C_6H_5CH:N.C_6H_3\left\langle\begin{array}{l}N=C.CH:CH.C_6H_5\\ \quad|\\ CO.N.N:CH.C_6H_5\end{array}\right.$$

. — 2-Methyl-3,7-diamino-4-quinazolone was boiled for a few minutes with excess of benzaldehyde. Upon cooling, a yellowish granular mass was obtained. This was extracted repeatedly with boiling alcohol, and the insoluble residue dried. This insoluble product melts at 238° (cor.) and is yellow in color.

Found: C, 79 1; H, 4 99; N, 12 29. Calculated for $C_{30}H_{22}ON_4$: C, 79 3; H, 4.85; N, 12.33.

It is readily soluble in chloroform, amyl alcohol or nitrobenzene; moderately soluble in acetone or benzene; but very difficultly soluble in ethyl alcohol or ether.

On concentrating the mother liquor from the above tri-benzal compound, a substance was isolated which on repeated crystallization from alcohol appeared in short, glistening, yellowish needles, melting fairly sharply at 196° (cor.).

Found: N, 15 47. Calculated for $C_{23}H_{18}ON_4$: N, 15.3.

This corresponds, therefore, to a di-benzal derivative. Its dilute alcoholic solution shows a greenish fluorescence.

In the mother liquor from this latter was found a third substance, crystallizing in dark yellow glistening, plates, melting at 172° (cor.), and also showing a greenish fluorescence in alcoholic solution.

Found: N, 15.43 Calculated for $C_{23}H_{18}ON_4$: N, 15.3.

The results would indicate that the above two substances are isomeric di-benzal derivatives, but the amounts isolated were insufficient for further investigation.

2-Styryl-3-benzalamino-7-acetamino-4-quinazolone.—2-Methyl-3-amino-7-acetamino-4-quinazolone was boiled with excess of benzaldehyde for five or ten minutes. The quinazolone dissolved readily in the hot aldehyde and the water escaped with a strong crackling noise. On cooling, the crude product separated in clusters of dark-yellow needles. If necessary, the excess of aldehyde can be blown out by a current of steam. Recrystallized from alcohol, the product forms yellowish needles, melting at 261° (cor.).

Found. N, 13.96. Calculated for $C_{25}H_{20}O_2N_4$. N, 13.72

It is practically insoluble in water, ether, or aqueous solutions of caustic alkalies, but dissolves easily in ethyl or amyl alcohol, acetone or nitrobenzene. Its alcoholic solution shows a greenish fluorescence. With cold concentrated hydrochloric acid, it turns a deep yellow, but does not dissolve to any great extent.

2-Styryl-3,7-diacetamino-4-quinazolone was prepared in a similar manner by condensing 2-methyl-3,7-diacetamino-4-quinazolone with benzaldehyde. Purified by crystallization from dilute alcohol, it melts at 283–4° (cor.), after preliminary softening a few degrees below this point.

Found: N, 15.56 Calculated for $C_{20}H_{18}O_3N_4$: N, 15.47.

It is soluble in water, ethyl or amyl alcohol, or chloroform, when hot, or in cold acetone, and dissolves with ease in hot acetone or nitrobenzene. With cold concentrated hydrochloric acid, it turns dark yellow and dissolves. It is somewhat tribo-electric.

VII. Condensation with 2-Methyl-3-amino-6-acetamino-4-quinazolone.

2-Styryl-3-benzalamino-6-acetamino-4-quinazolone was prepared like its 7-acetamino isomer by condensing the corresponding methylaminoacetaminoquinazolone with benzaldehyde. On boiling, the benzaldehyde solution changed from light yellow to dark reddish orange. When allowed to cool, a yellow crystallin cake resulted. The excess of benzaldehyde was blown out with steam, and the residual solid crystallized from alcohol. Short, yellow, silky needles were obtained, melting at 238–9° (cor.).

Found: N, 13.88. Calculated for $C_{25}H_{20}O_2N_4$: N, 13.72.

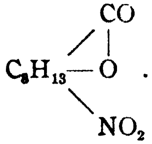
The compound is tribo-electric. It is darker yellow than its 7-acetamino isomer, more freely soluble in alcohol, and its alcoholic solutions show a stronger fluorescence.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. VI. ISOCAMPHOLACTONE.[1]

BY WILLIAM A. NOYES AND A. W. HOMBERGER.

Received October 13, 1910.

In a previous paper[2] we gave a brief report of a compound which we then considered to be a dilactone and to which we assigned the formula $C_8H_{13}O_4$. The compound is formed when isocampholactone is heated for some time with nitric acid and this led us to examine the substance qualitatively for nitrogen. For some reason, probably because the compound does not respond very readily to the usual test with metallic sodium, the result was negative, but after pursuing the study of the compound for some time further it was discovered that it has the composition of a nitrolactone,  $C_8H_{13}\begin{smallmatrix}\diagup CO \\ -O \\ \diagdown NO_2\end{smallmatrix}$. This has a molecular weight of 199 and does not agree with the determinations of the molecular weight reported in our first paper. The determinations by Victor Meyer's method were not, however, concordant and the low values found may have been due to partial decomposition.

The *isocampholactone* required for our experiment was prepared by decomposing the nitroso derivative of the anhydride of aminelauronic acid by boiling with a 10 per cent. solution of sodium hydroxide.[3] The specific rotation was determined in an 8.8 per cent. solution in alcohol, and gave $(\alpha)_D = -63.1^\circ$ at 28°. Taveau[4] gives the rotation in a 5 per cent. solution in alcohol as —60.7°.

Action of Ammonium Hydroxide on Isocampholactone.—Five tenths of a gram of isocampholactone were heated in a sealed tube in a water bath for 18 hours, till the lactone had passed into solution. The solution was evaporated in a vacuum desiccator and the residue purified by solution in absolute alcohol and precipitation with ligroin. It then melted at 137° and the analysis showed that it was the *ammonium* salt of the hydroxy acid corresponding to the lactone.

Calculated for $C_8H_{14}(OH)CO_2NH_4$: C, 57.14, H, 10.05; N 7.4.
Found: C, 57.20; H, 10.2 ; N, 7.26

---

[1] Abstract of a thesis presented by Mr. Homberger to the Graduate School of the University of Illinois in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[2] THIS JOURNAL, 31, 281.

[3] Noyes and Taveau, *Am. Chem. J.*, 32, 285; 35, 379

[4] *Am. Chem. J.*, 32, 290.

On standing in the air or on heating the salt passes back to isocampholactone.

Oxidation of Isocampholactone.—When isocampholactone is heated for 48 to 72 hours with nitric acid of sp. gr. 1.27 in a flask sealed to an upright condenser it is chiefly converted into the *nitroisocampholactone* which was described in our first paper as a lactone. If this is removed by dilution and filtration, the acid mother liquors leave on evaporation a viscous residue which crystallizes on standing.

Acid, $C_9H_{12}O_4$, melting at 138°.—After spreading the residue on porous porcelain to remove oily impurities it was crystallized from benzene. The analyses agree with the formula $C_9H_{12}O_4$.

Calculated for $C_9H_{12}O_4$ C, 58.67; H, 6.57.
Found. C, 59.09, 59.3, 59.0; H, 7.2, 7.02, 7.2.

The titration with standard alkali gave results corresponding to the molecular weights 186.0 and 186.9, for a monobasic acid. Calculated 184. The rotation of the acid in a 6 per cent. solution in alcohol was $(\alpha)_D = -42.05°$.

The Barium Salt, $(C_9H_{11}O_4)_2Ba$, was prepared by warming the acid with barium carbonate and water. It is easily soluble and separates without water of hydration.

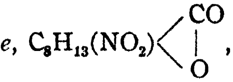
Found: Ba, 27.04. Calculated for $(C_9H_{11}O_4)_2Ba$, 27.29 per cent.

The *amide,* $C_8H_{11}O_2CONH_2$, was prepared by warming 0.5 gram of the acid with an excess of phosphorus pentachloride over a free flame in a test tube closed with a "Wallach's Aufsatz" until the mixture became liquid and pouring the cooled product into ammonium hydroxide. The amide which separated melts at 164°.

Calculated for $C_9H_{13}O_3N$: N, 7.65. Found: 7.84 per cent.

That the acid contains a lactone group was demonstrated by heating a portion of it for 12 hours on a water bath in a closed tube with somewhat more than two molecules of sodium hydroxide. Under these conditions 0.0569 gram neutralized 6.37 cc. of 0.1 *N* sodium hydroxide. Calculated for a bibasic acid, 6.18 cc.

It seems probable that this acid is formed by the oxidation of one of the methyl groups of isocampholactone.



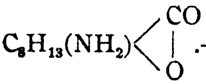
Nitroisocampholactone, $C_8H_{13}(NO_2)\left\langle\begin{matrix}CO\\ |\\ O\end{matrix}\right.$, is the principal product formed by the action of nitric acid (sp. gr. 1.27) on isocampholactone. It crystallizes from ligroin in needles. It is moderately soluble in ether and benzene. It melts at 122° and boils without apparent decomposition at 272°. The analyses were not altogether satisfactory, but leave no reasonable doubt as to the composition.[1]

---

[1] Schryver's analyses of nitrocampholactone (*J. Chem. Soc.*, 73, 562) were also unsatisfactory and somewhat similar to ours.

Calculated for $C_9H_{13}O_4N$: C, 54.29, ; H, 6.53, ; N, 7.04.
Found: C, 56 09; 55 89; H, 7.10, 7.25, N, 7 1.
54 85, 54 80; H, 7.12, 7.24; N, 7.2
54.81, 54 90, H, 7 12, 6 95.
54 90

The specific rotation of a 5.5 per cent. solution in alcohol is $(\alpha)_D$ = —85.4°.

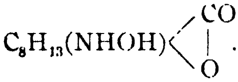

$C_8H_{13}(NH_2)\left\langle\begin{matrix}CO\\|\\O\end{matrix}\right.$

Aminoisocampholactone, $C_8H_{13}(NH_2)\left\langle\begin{matrix}CO\\|\\O\end{matrix}\right.$.—One gram of nitroisocampholactone was suspended in 4 cc. of concentrated hydrochloric acid, the mixture cooled with ice water and granulated tin, and, later, 2 or 3 cc. of hydrochloric acid added till all of the nitro compound passed into solution. Sodium hydroxide was then added in slight excess and the amino compound was extracted with ether. A large excess of sodium hydroxide seems to cause the decomposition of the product. The yield was about 0.35 gram. The aminolactone crystallizes in small, indefinit crystals, which melt at 84°.

Calculated for $C_9H_{15}O_2N$: C, 63 90; H, 8 87; N, 8.28
Found: C, 63 22; 63 10; H, 9 54; N, 8 10.

A solution of the aminolactone in absolute ether gave a precipitate of the chloride with dry hydrochloric acid. The aqueous solution of the chloride gave a yellow crystallin precipitate on standing for some time with chloroplatinic acid.

When the solution containing the amino compound was treated with a large excess of sodium hydroxide the amino compound was, apparently, decomposed and a relatively small amount of a compound melting at 152° was obtained. Owing to the small amount, this was not examined further.


$C_8H_{13}(NHOH)\left\langle\begin{matrix}CO\\|\\O\end{matrix}\right.$

Hydroxylaminoisocampholactone, $C_8H_{13}(NHOH)\left\langle\begin{matrix}CO\\|\\O\end{matrix}\right.$.—One gram of the nitroisocampholactone was dissolved in 8 cc. of glacial acetic acid and zinc dust added in small quantities, great care being taken to keep the solution cold. Zinc dust was added till the further addition caused no appreciable rise in temperature. The solution was then filtered from the excess of zinc dust and zinc acetate and the precipitate washed with a very little water. The solution was then made alkaline with sodium hydroxide, the temperature being kept low by cooling with ice. Care must be taken to avoid the use of too large an excess of sodium hydroxide. The best results were obtained by adding about 5 per cent. more than was required to neutralize the acid solution. The alkaline, turbid solution was then extracted with ether and the ethereal solution dried with sodium sulphate. The residue left on evaporating the ether was recrystallized from dry ether. It crystallizes in small, star shaped crystals, which melt at 144°.

Calculated for $C_9H_{15}NO_3$: N, 7.56. Found: N, 7.62.

Hydroxylaminoisocampholactone is slightly basic. It reduces Fehling's solution readily.

Decomposition of Nitroisocampholactone by Ammonium Hydroxide and by Sodium Hydroxide.—When nitroisocampholactone is treated with ammonium hydroxide or sodium hydroxide it is decomposed with the formation of compounds containing six atoms of carbon in the molecule. Carbon dioxide is also found but we have been unable to discover what becomes of the other two carbon atoms or to interpret the action which takes place.

Formation of the Amide, $C_5H_8NO_2CONH_2$.—This amide is formed when nitroisocampholactone is warmed with alcoholic ammonia or when it is allowed to stand, with frequent shaking, with cold concentrated aqueous ammonium hydroxide. The product was obtained by evaporation at ordinary temperatures in a strong current of air. The residue was recrystallized from benzene with the addition of a little petroleum ether. It melts at 96–97°.

Calculated for $C_6H_{10}O_3N_2$: C, 45.57, H, 6.3 ; N, 17.71.
Found: C, 45.7, 45.6; H, 7.0, 7.06; N, 17.6, 17.6
45.8, ; N, 7.14 ; N, 16.6.

Saponification of the Amide.—One-tenth of a gram of the amide was heated for 12 hours with 10 cc. of 0.5 *N* sodium hydroxide. The solution was then acidified and extracted with ether and the residue from the ethereal solution converted into the barium salt by warming with barium carbonate and water. Two samples of the salt prepared in this way lost on drying, 9.62 and 9.83 per cent. water. Calculated for $(C_6H_8NO_4)_2Ba$ $2^1/_2$ H_2O, 9.03 per cent. The anhydrous salt gave 30.34 and 30.40 per cent. Ba. Calculated 30.30 per cent. The acid recovered from the barium salt melted at 73° and was identical with the acid formed by the decomposition of nitroisocampholactone with sodium or barium hydroxide.

Acid, $C_5H_8O_2N.CO_2H$.—One gram of nitroisocampholactone was put in a test tube with 30 cc. of 0.5 *N* sodium hydroxide and allowed to stand with occasional shaking till all had dissolved. The solution was acidified with hydrochloric acid and extracted with ether. The ethereal solution was dried with sodium sulphate and the ether distilled. From the residue the barium salt of the acid was prepared by treatment with water and barium carbonate. After filtering from the excess of carbonate the solution was concentrated in a vacuum desiccator. The barium salt crystallizes well in needles which are moderately soluble in water. From the pure barium salt the acid was recovered by acidifying its solution with hydrochloric acid and extracting with ether. The acid is easily soluble in ether and in benzene, almost insoluble in ligroin. It melts at 73–74°. The acid appears to decompose and become semisolid on standing. Perhaps for this reason the analyses, especially the nitrogen determinations are not very satisfactory, but when these are taken with the titration values and the composition of the barium salt the formula assigned to the acid seems to be established.

Calculated for $C_8H_9O_4N$ C, 45.2 , H, 5.66 ; N, 8.80.
Found: C, 45.6, 45.8, 45.8, H, 5.9, 6.35, 6.4; N, 7.8, 7.5

Titration with 0.1 *N* sodium hydroxide gave a molecular weight of 162.9 and 163.0; with barium hydroxide 166. Theory 159

The Barium Salt, $(C_6H_8NO_4)_3Ba. 2\frac{1}{2} H_2O$ was analyzed completely because of the apparent instability of the acid. For the carbon determinations it was mixed with potassium dichromate to expel the carbon dioxide from the barium carbonate.

Calculated for $(C_8H_9NO_4)_2Ba.2\ 1/2\ H_2O$: C, 28.9 ; H, 4.2
Found: C, 29.2, 29.0; H, 4.8, 44.7.

The anhydrous salt gave 6.38 per cent. N, calculated 6.14

The salt lost 9.73 per cent water at 80°. Calculated for 2 1/2 H_2O, 9.04 per cent. The anhydrous salt gave 30.34 and 30.27 per cent Ba; calculated 30.30

From lack of time and the difficulty of preparing the material we have been unable to undertake experiments which might throw light on the structure of the acid.

URBANA, ILL.

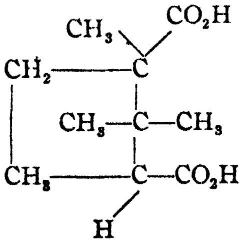
(CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. VII. DERIVATIVES OF ISOCAMPHORIC ACID; *l*-DIHYDROHYDROXYCAMPHOLYTIC ACID.

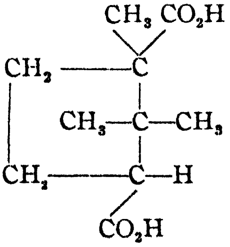
BY WILLIAM A NOYES AND LUTHER KNIGHT.

Received October 13, 1910.

It is generally assumed that *d*-camphoric acid and *l*-isocamphoric acid, which, as Aschan has shown, are each convertible into the other, are stereomers and differ only in that one is a *cis* and the other a *trans* form. This may be expressed by the following formulas:



d-Camphoric acid.



l-Isocamphoric acid.

Since methyl groups are known to shift from one carbon atom to another at much lower temperatures and under the influence of much less vigorous agents than those used to convert camphoric to isocamphoric acid the evidence for the structure of the latter does not appear to be altogether conclusive and it seemed to be of interest to obtain further evidence on this point. The study of the subject is far from complete but we have already obtained interesting and unexpected results.

Preparation of Isocamphoric Acid.—The method of preparing *l*-isocamphoric acid by heating *d*-camphoric acid with a mixture of hydrochloric and acetic acids[1] has been modified by largely increasing the proportion of camphoric acid used and also decreasing the amount of hydrochloric acid. The tubes are charged with 50 grams of *d*-camphoric acid, 25 cc. of glacial acetic acid and 2 cc. of concentrated hydrochloric acid (1.19). After sealing, the tubes are heated for ten hours at 170–180°. On account of the larger amount of acetic acid used the contents of the tubes are liquid after cooling. The acetic and hydrochloric acids are completely expelled by evaporation on the water bath and the residue after powdering finely is allowed to stand for an hour or longer with one-fourth of its weight of acetyl chloride (instead of the very large excess used by Aschan). The mixture is then treated with water and acid sodium carbonate, which dissolves the isocamphoric acid leaving the *d*-camphoric anhydride dissolved. From the filtrate the *l*-isocamphoric acid is precipitated by hydrochloric acid. In this manner 100 grams of the *d*-camphoric acid gave 37 grams of an acid containing 95.5 per cent. of isocamphoric acid as shown by the rotation. The camphoric anhydride which is recovered may be used for treatment with acetic and hydrochloric acids again, after crystallizing it from alcohol, and in this manner the conversion to isocamphoric acid may finally be made almost quantitative. The isocamphoric acid is easily purified by crystallization, best by dissolving it in a small amount of strong alcohol, adding 3 or 4 volumes of hot water, and allowing the solution to cool while exposed to the air, allowing a part of the alcohol to evaporate. The purified acid gave in a 10 per cent. alcoholic solution a rotation of $(\alpha)_D = -47.1°$, Aschan gives $-47.1°$.

α-Monomethyl Ester of l-Isocamphoric Acid.[2]—As with *d*-camphoric acid and its derivatives the secondary carboxyl of *l*-isocamphoric acid is much more easily esterified than the tertiary.[3] It is, accordingly easy to select conditions which will give chiefly the α-acid ester.

[1] Aschan, *Ber*, 27, 2005.

[2] Assuming that isocamphoric acid is stereomeric with camphoric acid, the secondary carboxyl is called α and the tertiary carboxyl β. See Noyes, *Am. Chem. J.*, 16, 500; 18, 686.

[3] Noyes, *Am. Chem. J.*, 18, 686.

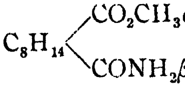
One hundred grams of isocamphoric acid, 400 cc. of methyl alcohol and 40 cc. of concentrated sulphuric acid were boiled for 20 minutes with a return condenser. The methyl alcohol was then distilled away under diminished pressure and the mixed esters which were precipitated with water were shaken with a strong solution of sodium carbonate which dissolved the acid ester. The neutral ester, which is always formed and which may become the principal product if the boiling is too long continued, was taken up with ether and distilled under diminished pressure. The acid ester was precipitated on adding hydrochloric acid to the sodium carbonate solution. The yield of acid ester may reach 95 per cent. of the theory.

The Dimethyl Ester of Isocamphoric Acid, $C_2H_{14}(CO_2CH_3)_2$, boils at 146° under 27 mm. pressure and has a specific gravity of 1.073 at 20° and 1.069 at 25°. Its specific rotation, $(\alpha)_D^{21°} = —65.2°$. In 10 per cent. alcoholic solution $(\alpha)_D = —63.6°$.

The α-Monomethyl Isocamphoric Ester prepared as described above was crystallized from petroleum ether. It crystallizes in needles which melt at 88°. In 10 per cent. alcoholic solution $(\alpha)_D = —57.9°$.

0.2340 g required for neutralization 10.85 cc. and 0.4640 g required 21.66 cc. 0.1 *N* KOH, calculated, 10.92 and 21.69 cc.

Amide of the α-Monomethyl Ester of Isocamphoric Acid,

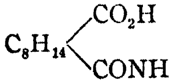


$C_8H_{14}\begin{cases}CO_2CH_3\alpha\\CONH_2\beta\end{cases}$.

—The acid methyl ester last described was mixed in a distilling bulb with an equal weight of phosphorus pentachloride, the mixture being cooled when more than a few grams are used. When the reaction is complete the phosphorus oxychloride is distilled away as rapidly and under as low a pressure as possible. The acid chloride is then poured carefully into a slight excess of ammonia (0.90), the latter being thoroughly cooled with ice or a freezing mixture. The amide obtained was crystallized from dilute alcohol. It crystallizes in plates on spontaneous evaporation of the alcohol. It melts at 157°. In 10 per cent. alcoholic solution $(\alpha)_D = —60.05°$.

The analysis gave 6.68 per cent. N; calculated, 6.57 per cent.

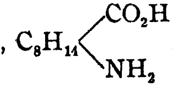
β-Isocamphoramidic Acid,



$C_8H_{14}\begin{cases}CO_2H\\CONH_2\end{cases}$

.—The amide of the monomethyl ester of isocamphoric acid was dissolved in alcohol, 10 per cent. in excess of one molecule of sodium hydroxide in a 30 per cent. solution was added and the mixture was heated for an hour or two on the water bath. Under these conditions the methyl ester is completely saponified while the amide group is scarcely affected. After removal of the alcohol by evaporation the β-isocamphoramidic acid was precipitated by hydrochloric acid and crystallized from dilute alcohol. It crystallizes in needles which melt at 165–166°.

The analyses gave 7.07 and 7.11 per cent. N; calculated 7.03 per cent. 0 0485 g took 2.3 cc. 0.1 N NaOH; calculated, 2 35 cc.

Isodihydroaminocampholytic Acid,  $C_8H_{14}\left<\begin{matrix}CO_2H\\NH_2\end{matrix}\right.$, was prepared from the isocamphoramidic by treating a solution of its sodium salt with a solution of sodium hypobromite.[1] The latter solution was prepared by aspirating the vapor of the measured or weighed amount of bromine through a 10 per cent. solution of sodium hydroxide.[2]

The Hydrochloride, $C_8H_{14}CO_2HNH_2.HCl$, was obtained by evaporating the acid solution to dryness and extracting the residue with strong alcohol. It is very easily soluble and crystallizes from concentrated solutions in needles. These do not melt at 250°.

0.0957 g. required 4.4 cc. 0.1 N $AgNO_3$; calculated, 4.5 cc.

The Lead Salt, $(C_8H_{14}NH_2CO_2)_2Pb$ was prepared by precipitation from an acetic acid solution and purified by washing with hot water in which it is almost insoluble.

The analysis gave 38.8 and 37.4 per cent. Pb; calculated, 37.8 per cent

The Free Isodihydroaminocampholytic Acid (not very pure) melts at 225–227°. When heated to 250 or 300° it gives an anhydride and the latter gives a nitroso compound which melted at 194° when freshly prepared but at 174–175° after standing overnight. These will be studied further.

When a solution of the hydrochloride of isodihydroaminocampholytic acid is treated with the calculated amount of a 20 per cent. solution of sodium nitrite introduced with a pipet beneath the former so that the two solutions mix by diffusion there are formed, apparently, a hydrocarbon, a lactone, *d*-campholytic acid and *l*-dihydrohydroxycampholytic acid. Only the last has been obtained in a fairly pure condition and fully identified.

The products at first obtained were taken up with ether and after removal of the latter the hydrocarbon, lactone and campholytic acid were distilled with steam. The lactone and campholytic acid were separated by means of sodium carbonate. The rotation of the campholytic acid finally obtained was +46° and it gives by titration results agreeing closely with the theory, but, in consideration of the small amount thus far obtained and of the fact that the rotation is not, as it should be, the same, though of sign opposit to that of *l*-campholytic acid[3] there is still some slight doubt as to the nature of the compound.

---

[1] Noyes, *Am. Chem. J.*, 16, 503.

[2] Dehn, THIS JOURNAL, 31, 526, footnote.

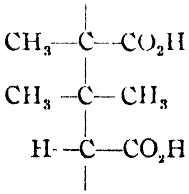
[3] Noyes and Phillips found —59.6° at 18°. *Am. Chem. J.*, 24, 291.

The l-Dihydrohydroxycampholytic Acid, $C_8H_{14}{<}^{CO_2H}_{OH}$, which remained behind after distillation of the other products with water vapor crystallized from water in granular crystals which melted at 132°. When these crystals were mixed with *d*-dihydrohydroxycampholytic acid, which melts at the same temperature, the melting point rose to about 170°, approaching that of the racemic acid.[1] The rotation in an aqueous solution containing 1.45 per cent. of the acid was $(\alpha)_D = -70.04°$. Noyes and Phillips[2] give +71.5 for the dextro acid.

0.1389 g. required 8.0 cc of 0.1 *N* NaOH, calculated, 8.07 cc

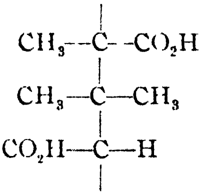
These results establish the identity of the acid as the levo form of dihydrohydroxycampholytic acid. The formation of this acid was wholly unexpected. If we represent the configuration of that part of the camphoric acid molecule containing the two asymmetric carbon atoms in the usual manner the results obtained establish the following relations as most probable:

d-Camphoric acid



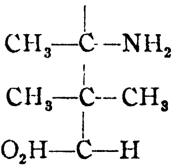
$$\begin{array}{c} | \\ CH_3-C-CO_2H \\ | \\ CH_3-C-CH_3 \\ | \\ H-C-CO_2H \\ | \end{array}$$

l-Isocamphoric acid.



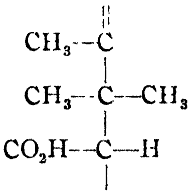
$$\begin{array}{c} | \\ CH_3-C-CO_2H \\ | \\ CH_3-C-CH_3 \\ | \\ CO_2H-C-H \\ | \end{array}$$

Isodihydroaminocampholytic acid.



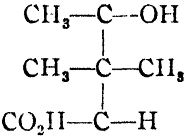
$$\begin{array}{c} | \\ CH_3-C-NH_2 \\ | \\ CH_3-C-CH_3 \\ | \\ CO_2H-C-H \end{array}$$

d-Campholytic acid.



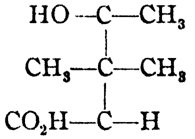
$$\begin{array}{c} \| \\ CH_3-C \\ | \\ CH_3-C-CH_3 \\ | \\ CO_2H-C-H \\ | \end{array}$$

Isodihydrohydroxycampholytic acid



$$\begin{array}{c} CH_3-C-OH \\ | \\ CH_3-C-CH_3 \\ | \\ CO_2H-C-H \end{array}$$

l Dihydrohydroxycampholytic acid.



$$\begin{array}{c} HO-C-CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ CO_2H-C-H \end{array}$$

The formation of *d*-campholytic is entirely in accord with the theory, since in this acid one of the asymmetric carbon atoms of the isocamphoric acid has lost its asymmetry through the formation of the double union. The formation of *l*-dihydrohydroxycampholytic acid is not so easily explained. From its method of formation we should expect for this the configuration of an isodihydrohydroxycampholytic acid which is not the optical antipode of *d*-dihydrohydroxycampholytic acid, but which has the methyl and hydroxyl groups reversed. This recalls the fact that *l*-campholytic acid adds hydrobromic acid to form *d*-bromodihydrocampholytic acid,[1] taking up the hydrobromic acid asymmetrically. The *d*-campholytic acid would, of course, give *l*-dihydrohydroxycampholytic acid in a similar manner. It is probable from this that the left form of the hydroxy acid is more stable than the expected isodihydrohydroxycampholytic acid and that a portion of the latter is transformed to the former by the action of the nitrous acid—or it may be that *d*-campholytic acid is formed as an intermediate product and that this adds water to form the *l*-dihydrohydroxycampholytic acid.

---

[1] Noyes and Blanchard, *Am. Chem. J.*, **26**, 287.

[2] *Am. Chem. J.*, **24**, 290.

The study of these compounds will be continued.

URBANA, ILL.

[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY INVESTIGATIONS.]

SOME ACID CONSTITUENTS OF SOIL HUMUS.[2]

BY OSWALD SCHREINER AND EDMUND C. SHOREY.

Received September 27, 1910

The complex character of the humus or organic matter of the soil need hardly be emphasized here, nor need the complexity of the so-called humic acid be again mentioned other than to remark that so many organic compounds, neutral, basic and acid, have been isolated therefrom in these researches that its claim to chemical unity is absolutely refuted and its non-existence proved. The present paper is a further contribution to the definit knowledge of the chemical nature of this organic soil complex and gives a description of several acids isolated therefrom. The isolation of other acid substances from soils, picolinecarboxylic acid, dihydroxystearic acid and agroceric acid, are reported in earlier papers.[3]

α-Monohydroxystearic Acid, $C_{18}H_{36}O_3$.—When the humus extract of a soil obtained by extraction with dilute alkali is acidified, a brown, flocculent precipitate of the so-called humus substances is formed. If this precipitate is separated by filtration, washed and treated while still moist with boiling 95 per cent. alcohol, a portion of the precipitate goes into solution. The amount of the humus precipitate so dissolved varies with the character of the soil treated, but the alcoholic solution obtained in this way is always dark-colored. On careful evaporation of this alcoholic solution, adding water to keep the volume constant until the alcohol is removed, there is formed a brown or reddish brown precipitate which can be separated by filtration. When so separated, washed and dried, it is in the form of resinous lumps or powder, varying in color, melting point and composition, with the soil from which it was obtained.

On extracting this resinous material with petroleum ether there is obtained an extract generally colorless or light-colored, which on evaporation of the petroleum ether leaves a residue which may vary from an oily, semi-solid mass to a waxy solid. This residue is generally wholly soluble in hot alcohol. From this alcoholic solution there sometimes separates on cooling a white or yellowish microcrystallin mass or powder which in the case of one soil has been identified as α-hydroxystearic acid.

---

[1] Noyes and Phillips, *Am. Chem. J.*, 24, 24, 291.

[2] Published by permission of the Secretary of Agriculture.

[3] THIS JOURNAL, 30, 1295, 1599 (1908); Bureau of Soils, U. S. Dept. Agr. *Bull.* 53, (1909).

The soil from which this compound was obtained was a sample of Elkton silt loam, a type covering a considerable area in Maryland. This soil is almost white in color, high in clay and silt and contains 0.53 per cent. organic carbon and 0.066 per cent. nitrogen. The sample examined was one of several hundred pounds obtained from the eastern shore of Maryland.

This soil when treated with 2 per cent. sodium hydroxide solution yields an extract much darker than might be expected from a soil so light in color. From this brown alkaline extract there is precipitated on acidifying with sulphuric acid a brown, flocculent mass. On separation of this by filtration, washing and treating with boiling 95 per cent. alcohol, there is obtained an alcoholic solution nearly as dark in color as the original alkaline extract. The precipitate formed by evaporation of the alcohol and addition of water was, after filtration, washing and drying, a brown mass easily pulverized.

Extraction of this brown powder with petroleum ether and evaporation of the solvent left an oily, semi-solid, light-yellow mass, which was completely soluble in hot 95 per cent. alcohol. On cooling, this alcoholic solution there separates a yellow, microcrystallin powder, which after separation by filtration, washing with cold alcohol, dissolving again in hot alcohol, and repeating the separation several times, can be obtained free of color and of constant melting point.

The substance so obtained melts at 84-85°, is soluble with difficulty in cold alcohol, readily in hot alcohol, cold ether or petroleum ether. It crystallizes usually in small irregular leaflets, but can be crystallized from alcohol by very slow cooling, in six-sided plates. It forms salts with alkalies soluble in water and can be obtained from such solution unchanged by acidifying and extracting with ether.

The analysis of this compound gave the following:

Calculated for $C_{18}H_{36}O_3$: C, 72.00; H, 12.00
Found: C, 72.09; H, 12.17

This composition corresponds with that of the monohydroxystearic acids, two of which are known, designated α and β, respectively, and having the formula $C_{18}H_{36}O_3$. The properties of the acid isolated from the soil fix it as the α acid. The α acid is much less soluble in alcohol than the β acid and the β acid, moreover, forms an anhydride on heating with strong hydrochloric acid, which is not the case with the α acid nor the acid from the soil. The melting points of the α and β acids are so nearly the same that this property cannot be used to distinguish between them. The melting point of the pure α acid artificially prepared remained unchanged on mixing with the acid from the soil. This fact, together with the composition found and sparing solubility in alcohol and failure to form an anhydride, is sufficient to establish the identity of the acid from the soil as α-monohydroxystearic acid.

α-Hydroxystearic acid is easily made in the manner described by Sadomsky.[1] When stearic acid is treated with red phosphorus and bromine, α-bromostearic acid is formed. On heating this with alcoholic potash the potassium salt of α-hydroxystearic acid is formed and on acidifying the aqueous solution of this salt the acid is set free and can be extracted with ether.

α-Hydroxystearic acid is not known to occur in any natural animal or vegetable product and up to the present has been isolated from only one soil.

Two hydroxy acids of the fatty series have been isolated from soils, but neither are known as natural products. These are α-hydroxystearic acid and the dihydroxystearic acid previously described.[2] Both must be looked on at present as the products of the action of microorganisms, probably fungi, on some of the organic matter known to be of plant or animal origin.

While at present little is known of the processes by which these compounds are formed in the soil and little can be said that is not of a speculative nature, it may be of interest at this point to note the laboratory methods by which hydroxy acids are formed. Three general methods are known by which the hydroxy acids are formed from the corresponding acid. These are: Making a halogen substitution product and treating this with silver oxide and water; making an amino derivative and treating this with nitrous acid; and making a sulphonic acid derivative and treating it with caustic potash.

In attempting to find a parallel between these reactions and the processes likely to take place in the soil, the second method seems to be the only one that offers any foundation for a theory. It is known that amino compounds result from the decomposition of more complex nitrogenous compounds and may possibly be formed or built up by the action of ammonia, which is commonly formed in soils. Nitrous acid, as the result of denitrification or as the first stage in the change of ammonia into nitrates, is formed in nearly all soils and would supply the reagent required in the second stage of the reaction.

In addition to these purely chemical methods of formation, there are to be considered the biological formations by fungi or bacteria, but this would lead somewhat afield from the purposes of the present article.

---

[1] *Ber.*, 24, 2388 (1891).

[2] Bureau of Soils, U. S. Dept. Agr., *Bull.* 53, (1909). THIS JOURNAL, 30, 1599 (1908).

While α-hydroxystearic acid is not known as a natural product, it must be remembered that natural fats and oils are usually complex mixtures of glycerides and that the chemistry of such glycerides as occur in these products in small amounts is very incomplete. More complete chemical knowledge of the natural fats and oils may show the presence of α-monohydroxystearic acid. The method of its laboratory preparation does not suggest any possible parallelism in the soil as was the case when the origin of dihydroxystearic acid was under discussion.

In the earlier literature of the hydroxystearic acids there is some confusion of nomenclature, as well as disagreement regarding their constitution. The β acid described by Saytzeff[1] was designated as the α acid by Geitel.[2] The designations α and β acid seem to have been primarily used to distinguish isomers, the constitutions of which were not known. The constitution, as now accepted and established by Shukov and Shestakov[3] is not in harmony with the common meaning of α and β designations. In the simple hydroxy fatty acids the term α is applied to that acid having the hydroxyl group next the carboxyl group; for example, α-hydroxypropionic acid (lactic) is represented thus: $CH_3.CHOH.COOH$; the term β is applied to that acid having the hydroxyl on the second carbon atom; for example, β-hydroxypropionic acid (hydracrylic) is represented thus: $CH_2OH.CH_2COOH$. The constitution of the α and β-hydroxystearic acids is represented as follows: α acid, $CH_3(CH_2)_6CH.OH(CH_2)_9COOH$; β acid, $CH_3(CH_2)_7CH.OH(CH_2)_8COOH$. In neither case is there α or β structure. The authors in discussing these formulas used the designations: 1.11 for the α acid, and 1.10 for the β acid, 1 being the carbon atom of the carboxyl group and 10 and 11 the carbon atoms counting from 1 to which the hydroxyl group was attached. Since, however, these acids are still generally described and referred to in the literature as α and β, these terms have been used in this paper with this explanation.

Paraffinic Acid, $C_{24}H_{48}O_2$.—The cold alcoholic solution from which α-hydroxystearic acid has separated in the manner just described is yellow in color and evaporation of the alcohol leaves a semi-solid, oily mass. On standing some time crystals form in this mass, but the nature of the material was such that they could not be separated without great loss and so this was not attempted. The oily mass was dissolved again in alcohol and an alcoholic solution of lead acetate added. This gave a yellow precipitate which was separated by filtration, washed with alcohol, suspended in alcohol and treated with hydrogen sulphide. After separation from the lead sulphide the alcoholic solution was allowed to evaporate slowly, leaving a somewhat waxy mass of leaflets. This mass was purified by dissolving again in alcohol and repeating the operation of precipitation with lead acetate and finally drying on a porous plate. The body so obtained was light yellow in color and melted at 45-48°. Analysis gave the following figures:

---

[1] *J. prakt. Chem* (2), 35, 369 (1887).

[2] *Ibid.* (2), 37, 53 (1888).

[3] *Ibid.* (2), 67, 414 (1903).

Calculated for $C_{24}H_{48}O_2$: C, 78.20; H, 13.00.
Found: C, 78.40; H, 13.29.

This composition, the melting point and physical properties correspond with paraffinic acid, $C_{24}H_{48}O_2$, described by Pouchet[1] as obtained by the action of fuming nitric acid on paraffin.

The research of Pouchet on which alone the existence of paraffinic acid rests is, as published, inconclusive as to its being a definit chemical compound. The quantity of this substance obtained from the soil was insufficient for any extended research and so far the character of the compound obtained from paraffin has not been studied except that the following facts were established. Paraffin was treated with fuming nitric acid in the manner described by Pouchet and a compound obtained having the properties and composition stated by him. Elementary analysis of this substance gave the following figures:

Calculated for $C_{24}H_{48}O_2$: C, 78 2; H, 13 0.
Found C, 78 1; H, 13 3.

The properties and composition of this compound corresponded with those of the substance obtained from the soil and there is little doubt that whatever may be the nature of the two substances, they are identical. With this understanding, the name paraffinic acid is applied to the soil compound. This body has so far been obtained from but one soil, the Elkton silt loam already described. A number of soils have been examined that gave at the point where paraffinic acid was obtained in the case of the Elkton silt loam a precipitate with alcoholic lead acetate, but the quantity of material has been either too small for identification or has had other properties and composition.

Very little can be said regarding the possible origin of paraffinic acid in the soil. Several solid hydrocarbons of the paraffin series have been shown to occur in plants and may therefore be a part of the organic matter added to the soil. Oxidation of these in the soil might give rise to the substance found.

It may be noted in this connection that it is well established that paraffin can be oxidized in the laboratory, but usually by rather vigorous treatment. Gill and Mensel[2] found that on treating paraffin with dilute nitric acid or chromic acid it was oxidized to cerotic acid, $C_{27}H_{54}O_2$, acetic acid and succinic acid. Pouchet in the research referred to found succinic acid in addition to paraffinic acid, but no cerotic acid.

---

[1] *Bull. soc. chim.*, 23, 111 (1875).

[2] *Zeit. Chem.*, 1869, 65.

Lignoceric Acid, $C_{24}H_{48}O_2$.—When a soil high in organic matter is carefully heated in a closed tube, there is obtained a dark-colored, tarry distillate, which in some cases sets on cooling to a semi-solid, crystallin mass.

A peat soil containing 27 per cent. of organic carbon treated in this way gave a distillate of this character in considerable quantity. The semi-solid mass on washing with cold alcohol was freed from much of its color with little loss of solid matter. The material so washed was completely soluble in hot alcohol from which it separated on cooling in microcrystallin form. On repeating this solution and separation several times the material was obtained nearly free of color. Treatment at this stage with cold petroleum ether removed the remaining color and a small quantity of oily matter. The body after this purification melted at 80–81°, was soluble in ether and hot alcohol, little soluble in cold alcohol and insoluble in water. Its elementary composition was found to correspond to the formula, $C_{24}H_{48}O_2$.

Calculated for $C_{24}H_{48}O_2$	C, 78 2; H, 13 0
Found	C, 78 1; H, 13 2

The compound dissolved in aqueous alkalies and was set free from such solution unchanged on addition of a mineral acid. The properties, melting point and composition indicate the identity of this compound as lignoceric acid first described and obtained by Hell and Hermanns[1] from the solid residue or "paraffin" of beechwood tar. It is also found[2] as a glyceride in peanut oil.

It is generally assumed that the lignoceric acid found in wood tar is the result of decomposition effected by the method of treatment and that it does not occur as such in the wood. In the case of the soil, however, certain observations indicated that this might not be the case. It was observed that if the soil was heated to a high temperature or the heating done rapidly the yield of solid matter in the distillate was very small. When the heating was done carefully and the temperature raised only to the point where a distillate could be obtained, the solid product seemed to be the result of distillation directly from the soil and when the operation was carried on in a glass tube such distillation could actually be observed, the melted distillate collecting on the upper, cooler side of the tube and being driven forward as heat was applied, just as water would be. It was also found that the purified lignoceric acid obtained from the soil in the manner described could by careful heating be distilled with little or no decomposition.

---

[1] *Ber.*, **13**, 1713 (1880).

[2] Kreiling, *Ber.*, **21**, 880 (1888).

With the object of extracting the lignoceric acid from the soil if it existed as such, the soil was treated with boiling 95 per cent. alcohol, the extract filtered hot and allowed to cool. On cooling, a voluminous precipitate separated from the dark-colored extract. This was separated by filtration and purified by dissolving several times in hot alcohol from which it separated on cooling and finally by washing with cold petroleum ether. The compound so obtained corresponded in all properties with that obtained by distillation. It melted at 80-81° and elementary analysis gave the following figures:

Calculated for $C_{24}H_{48}O_2$: C, 78.2; H, 13.0.
Found: C, 78.2; H, 13.8.

The identity of the two compounds obtained from the soil by distillation and by extraction with hot alcohol is thus established. It follows that lignoceric acid exists in the soil as such.

Regarding the source of the lignoceric acid in the soil there are two possibilities suggested by our knowledge of the compound. It is, as has been already stated, present in peanut oil as a glyceride and may be a component of other vegetable oils and be somewhat widely distributed in plants in small amounts, in which case it might occur in the soil as a residue of the decomposition of such glycerides.

Lignoceric acid is obtained by the distillation of wood, presumably through the decomposition of woody tissue. It is possible that similar decomposition through the agency of microorganisms may take place in the soil.

BUREAU OF SOILS, WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY INVESTIGATIONS.]

PENTOSANS IN SOILS.[1]

BY EDMUND C SHOREY AND ELBERT C. LATHROP.

Received September 28, 1910.

Carbohydrates, represented by sugars, starch and compound celluloses, make up by far the greater portion of the organic substance of plants and so form the greater portion out of which soil organic matter is made. The extreme susceptibility of these substances to fermentation or decomposition by microörganisms renders them, probably, the most unstable organic material added to soils. Sugars and starch are used by a great variety of bacteria and fungi as food and no doubt disappear as such long before the cell tissues break up and become part of the soil. The cell wall and fibrovascular tissues are made up for the most part of a complex compound containing a carbohydrate or cellulose radical. These resist the action of microörganisms longer and in the breaking up of the tissues due to the decay of the least resistant portions, this complex probably gets into the soil to some extent unchanged.

---

[1] Published by permission of the Secretary of Agriculture.

The products of decomposition of such carbohydrates as starch and sugars, are fairly well known and are for the most part simple compounds, such as alcohol, acetic acid and carbon dioxide. The more resistant complexes, the so-called compound celluloses, contain other groups in addition to the carbohydrate radical and can give rise in decay to a great variety of products some of them still quite complex, but resistant to further action of bacteria or fungi. Because of this complexity of the material itself and of its decomposition products, the character of the changes which take place in the decay of this material, either in or out of the soil, is very imperfectly known.

The isolation of carbohydrates from soil is at present confined to a single compound, a pentosan or a substance yielding a pentose sugar.

Nearly all soils when boiled with hydrochloric acid of moderate strength give furfural. The evolution of furfural when an organic mixture is heated with hydrochloric acid is usually regarded as evidence of the presence of pentosans. Pentosans are substances of a gummy nature and unknown constitution for which the formula $C_5H_8O_4$ is usually given; they gives on hydrolysis with acids pentose sugars, $C_5H_{10}O_5$, which are definit crystallin compounds of known constitution. These pentose sugars on further heating with acids give furfural, the amount of furfural being proportional to the amount of pentosan or pentose. Based on this fact a method has been devised for determining the pentosan by determining the amount of furfural obtained under certain conditions. This method is adopted as a provisional one by the Association of Official Agricultural Chemists.[1]

The method, when applied to soils, generally gives weighable quantities of the phloroglucide, the form in which the furfural is determined. The figures given below show results obtained by this method applied to ten soils of widely different types and character of organic matter. Ten grams of soil were used, boiled with 12 per cent. hydrochloric acid and the distillation carried on in the usual manner until there was no further evolution of furfural, which was usually the case when the distillate amounted to 300 or 400 cc. The furfural was determined as phloroglucide and the calculation made according to the formula in the provisional method cited.

The figures given here illustrate well, perhaps better than any others available, the great variation of organic matter in soils. In these ten soils selected somewhat at random the pentosan carbon per 100 of total carbon varies from 1.30–28.53, while the third lowest result, 1.83, was obtained from a soil containing the largest quantity of organic matter.

---

[1] Bureau of Chemistry, U. S. Dept. Agr., *Bull.* 107, p. 54. (Revised),

Soil.	Per cent. total carbon	Per cent. pentosan.	Per cent pentosan carbon.	Pentosan carbon per 100 of total carbon.
Elkton silt loam.	0.522	0.176	0.079	15.13
Sassafras silt loam	0.315	0.055	0.025	7.93
Chester silt loam	1.510	0.182	0.083	5.49
North Carolina peaty soil.	27.102	1.090	0.495	1.83
Marshall loam.	6.971	2.750	1.249	17.93
California peaty soil.	11.478	0.341	0.150	1.30
Norfolk fine sandy loam.	0.822	0.027	0.012	1.46
Santa Paula, Cal., loam	1.308	0.061	0.028	2.14
Portsmouth loam.	3.854	0.219	0.099	2.57
Susquehanna clay loam	1.048	0.659	0.299	28.53

The Marshall loam containing the largest quantity of pentosan, 2.75 per cent., was selected for further investigation. The soil was from North Dakota and the sample was taken from a field that had grown flax for a number of years. There had been no direct addition of straw or other pentosan-containing material other than that incidental to the growing and harvesting of the crop. An alkaline extract of this soil was made by treating it for several hours with 2 per cent. sodium hydroxide, the dark-colored extract was siphoned off and the humus compounds precipitated by acidifying with acetic acid, the filtrate made neutral and filtered from the precipitate formed. Lead acetate in excess was added to the neutral filtrate, resulting in the formation of a heavy brown precipitate and the removal of nearly all the color from the solution. To the filtrate from this precipitate dilute ammonia was carefully added, when a light yellow, voluminous precipitate was formed. This, after washing, was suspended in water and treated with dilute suphuric acid, avoiding excess. The lead sulphate was removed by filtration and the filtrate concentrated to a small volume. To this solution three volumes of 95 per cent. alcohol were added, when a gummy precipitate was formed which after washing with alcohol dried to a hard, translucent mass. This mass contained traces of lead which it retained very persistently. It was soluble in alkalies and formed an opalescent mucilage with water. On heating with 12 per cent. hydrochloric acid, furfural was given off freely and on heating with phloroglucinol and hydrochloric acid the characteristic purple color reaction for pentose sugars was obtained. On digesting for some time with sulphuric acid of moderate strength and neutralizing, a solution was obtained which reduced Fehling's solution and gave an osazone melting at 160–161°. On treating with cadmium carbonate and bromine according to the method of Bertrand,[1] the characteristic crystals of the double salt cadmium xylonate and cadmium bromide were obtained, showing the presence of xylose as one of the products of hydrolysis of the substance isolated from the soil. Tests made for the presence of other pentose sugars gave negative results.

---

[1] *Bull. soc. chim.*, [3] 5, 556 (1891).

The quantitative method of determining pentosan depends as has been noted on the formation of a pentose from the pentosan and the formation of furfural from the sugar on further heating with acid. In the cell wall material which makes up such a large portion of the organic matter of plants no doubt there is a pentosan compound present, either as such, or as part of the complicated molecule of lignocellulose, for a crude pentosan can be prepared from such material. In the case of the Marshall loam such a crude pentosan was obtained and was probably present as such in the soil as a plant residue. In the case of soil organic matter in general, however, it cannot be assumed that the formation of a pentose sugar and from it furfural, necessarily indicates the presence of a pentosan as such. Pentose sugars are part of the complicated molecule of nucleoproteins and phosphatides and are split off from these on heating with acids. The nucleoproteins are characteristic of tissues in which nucleated cells are abundant and those of animal origin have been especially studied. The investigation of those of plant origin is not so thorough, but there is every evidence that the parts of plants rich in cells are also rich in nucleoproteins and this compound and its decomposition products must contribute to the organic matter of the soil.

With this in mind it is evident that a determination of pentosan in soil by the method in general use is simply the determination of the furfural that may arise from a pentosan, a pentose, or a pentose-yielding material other than a pentosan.

In the light of our present knowledge of pentosans and pentose-yielding material, their presence in a soil must be regarded either as a plant residue, such as a portion of the lignocellulose, which has resisted decomposition, or as products of decomposition of complicated compounds such as nucleoproteins.

BUREAU OF SOILS, WASHINGTON, D. C.

[FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY OF THE DEPARTMENT OF ANIMAL HUSBANDRY OF THE UNIVERSITY OF ILLINOIS.]

ON THE PRESERVATION OF FECES.

BY PAUL E HOWE, T. A RUTHERFORD AND P. B. HAWK

Received September 27, 1910

Fresh feces lose nitrogen when subjected to a drying process, even when such process is carried out under the most carefully controlled conditions. Of late years this fact has come to be generally recognized and consequently various schemes have been adopted in the attempt to determin the amount of this lost nitrogen in order that a correcting factor might be applied. None of these forms of manipulation, so far as we are aware, has proved entirely satisfactory. As a result of a series of tests Zaitschek[1] concluded that the loss of nitrogen in drying feces was greater for the feces of carnivora than for those of the herbivora. He further found that drying feces with added acid did not always wholly prevent a loss of nitrogen and that entirely accurate results could only be obtained by determining the nitrogen content in several samples of fresh feces. The extent of the nitrogen loss, according to this investigator, depends on the quantity of non-protein nitrogen present, as well as upon the moisture content of the feces.

In our experiments the feces were collected in the ordinary friction-top paint pail which had previously been rinsed with a 10 per cent. alcoholic solution of thymol and subsequently dried. During the preservation period these pails were kept in a refrigerating room. The feces were analyzed for nitrogen and moisture. In some of the tests, the data from which are given below in tabular form, the stools were analyzed immediately after defecation and at short intervals thereafter. In other tests the stools were collected from a subject through a period of eight days and this carefully mixed eight-day sample was then subjected to analysis, the initial analysis being followed by others at long intervals. In some instances the tests covered a period of two hundred and forty-eight days after the dropping of the stool.

In Table I we have data from two samples collected from two different individuals living on similar diets, the feces being collected through an eight-day period as just indicated. An examination of the data from stool No. 1 shows that there was practically no change in the nitrogen value of the sample even after 158 days in the refrigerating room. From this time to the end of the experimental period of 248 days there was a slight lowering of the nitrogen content. In the case of the moisture content of this stool the data indicate that there was practically no change in the moisture value for a period of twenty-one days. On the one hundred and fifty-eighth day the moisture had increased about 3 per cent. Unfortunately no analyses were made during the period intervening from the 21st to the 158th day. Stool No. 2 analyzed at the same intervals as stool No. 1 yielded similar data.

Data from the analyses of three individual stools dropped by three men living on different diets are given in Table II. The initial analysis was in each instance made seven hours after the stool was passed, this first analysis being followed by other analyses at intervals of 2, 4 and 8 days. In one instance (stool No. 4) the final analysis was made on the 83rd day. Each stool yielded a very uniform series of values for both nitrogen and moisture throughout the experimental period of eight days. At the 83rd day stool No. 4 was found to have gained moisture (5–6 per cent.) and to possess a lower nitrogen content. In Table III are given data from 3 other individual stools which were collected under similar conditions as those mentioned in Table II and dropped by the same individuals. The procedure in the case of the stools differed from that adopted in the case of the stools mentioned above in that the first analysis was made upon the fresh stool. The stools were passed, immediately mixed, sampled and portions weighed out for analysis. The analysis of the fresh feces was followed by the further examination of the stool at intervals of 2, 5 and 7 days. An examination of the table will show a most satisfactory uniformity in the values obtained from the different analyses.

---

[1] *Arch ges. Physiol.*, 98, 595 (1903).

Data from composit stools are again given in the Table IV. This table includes data from 6 composit stools analyzed at intervals of 8, 43 and 92 days. These samples were from 6 different men living upon a similar diet, the individuals being different from those previously mentioned. At the end of the forty-third day the nitrogen and moisture values (with the exception of those of stool No. 10) were found to be rather uniform with those obtained at the initial analysis.

Conclusions.

I. The method of feces collection and preservation which involves the use of friction-top pails is very satisfactory for the following reasons:

1. It permits of the analysis of the *fresh* feces.

2. It prevents loss of moisture.

3. It maintains the nitrogen content practically unaltered for at least *twenty days* and frequently for a much longer period.

4. It eliminates all loss of material since the feces are not transferred to any other receptacle before they are thoroughly mixed for analysis.

II. It is preferable to make the analysis on the *fresh* feces, since this procedure does away with all drying processes and hence eliminates the loss of nitrogen which invariably accompanies such drying.

TABLE I. – COMPOSIT STOOLS.

	8 days.	16 days	10 days.	21 days	158 days.	248 days.
Stool No 1.						
Nitrogen (moisture-free), per cent	2.396	2.374	2.403	2 362	2.340	2 269
Moisture, per cent	70.40	70 87	70 11	70 60	73 47	74.03
Stool No. 2.						
Nitrogen (moisture-free), per cent	1.954	2.036	2 049	2 033	1.892	1.823
Moisture, per cent	76 87	76 19	76 64	76.64	79 86	80.58

TABLE II.—INDIVIDUAL STOOLS.

	7 hours.	2 days.	4 days.	8 days	83 days.
Stool No. 3.					
Nitrogen (moisture-free), per cent	2.179	2.275		2.263	
Moisture, per cent	75.36	75.24		74.66	
Stool No. 4.					
Nitrogen (moisture-free), per cent	2.312	2.387	2.343		1.641
Moisture, per cent	73.28	73.14	73.44		79.18
Stool No 5.					
Nitrogen (moisture-free), per cent	1.582	1.597	1.622	1.618	
Moisture, per cent	74.85	74.62	74.40	74.93	

TABLE III.—INDIVIDUAL STOOLS.

	Fresh.	2 days.	5 days.	7 days.
Stool No. 6.				
Nitrogen (moisture-free), per cent		1.854	1.816	1.843
Moisture, per cent	77.62	76.61	77.26	76.44
Stool No. 7.				
Nitrogen (moisture-free), per cent	1.491	1.471	1.470	1.473
Moisture, per cent	80.06	80.48	80.16	80.18
Stool N. 8.				
Nitrogen (moisture-free), per cent	1.319	1.347	1.295	1.335
Moisture, per cent	76.49	76.16	76.04	75.95

TABLE IV.—COMPOSIT STOOLS.

	Per cent. nitrogen (moisture-free basis).		
Stool No.	8 days	43 days.	92 days.
9	1.913	1.901	1.788
10	1.863	1.740	1.848
11	2.179	2.270	..
12	2.127	2.194	2.068
13	1.730	1.736	1.663
14	1.629	1.631	1.743

[FROM THE LABORATORIES OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS AND THE UNIVERSITY OF PENNSYLVANIA.]

STUDIES ON WATER DRINKING.[1] III. ON THE URIC ACID ELIMINATION FOLLOWING COPIOUS WATER DRINKING BETWEEN MEALS.

BY S. A. RULON, JR., AND P. B. HAWK.

Received October 18, 1910.

The present paper embraces a report of two metabolism studies made upon two individuals, the topic under consideration being the determination of the influence of large volumes of water taken *between* meals upon the uric acid output. The subjects were young men 24 and 29 years of age respectively. They were placed upon uniform diets containing a small amount of water and were brought into nitrogen equilibrium, after which an interval elapsed during which large volumes of water were daily added to the uniform diet, the added water being taken *between* meals. This period of high water ingestion was then followed, in each instance by a period throughout which the uniform diet and low water ration of the preliminary interval were fed. In the first experiment the three periods of the test were 3, 4, and 2 days in length respectively, whereas in the second experiment the periods were 3, 2, and 4 days in duration. The daily diet, during the first study, consisted of 2100 grams of whole milk, 120 grams of butter and 300 grams of crackers, this ration being divided into 3 equal portions and fed at the customary intervals. The ration of the second study was 1800 grams of whole milk, 75 grams of butter and 330 grams of crackers. During the interval of copious water ingestion of the first experiment, the volume of water daily ingested was 5900 cc. as against an ingestion of 400 cc. per day during the preliminary and final periods. These volumes were 5,000 cc. and 500 cc. respectively in the second experiment. In other words the water ingestion was increased $5^1/_2$ liters in the first study and 5 liters in the second study. The body weights of the subjects were about the same (60.6 kg. and 61.5 kg.). During all of Experiment II and for 3 days of Experiment I, the urine was collected in 24-hour samples. The urine specimens for the remaining days of the first experiment were daily collected in 5 sub-periods, there being four $3^1/_2$-hour periods and one ten-hour period. The $3^1/_2$-hour periods began at 8 a.m. and extended from that hour until 10 p.m., the 10-hour period extending from 10 p.m. until 8 a.m. the following day. The urine samples were preserved by thymol powder. Uric acid was determined by the Folin-Shaffer method.[1]

---

[1] For I and II of this series of studies see Hawk, *University of Penn. Med. Bull.*, 18, 7 (1905); and Fowler and Hawk, *J. Exp. Med.*, 12, 388 (1910), respectively.

Copious Water Drinking and Uric Acid Output.

The data from the first experiment are given in Table I. An examination of that table shows that there was 0.319 gram of uric acid excreted upon the first day of the experiment and that this was followed on the remaining two days of the preliminary period by daily eliminations of 0.294 gram and 0.267 gram respectively. When the large volume of water was introduced into the organism, however, there was a decided lowering of the uric acid values. The data indicate that the quantitative examination of the urines for the 4 days of copious water ingestion yielded values of 0.195, 0.131, 0.150 and 0.148 gram respectively. The final period in which small amounts of water were again daily ingested was accompanied by a return to the normal uric acid level of the preliminary period. These data would seem to indicate, then, that the ingestion of large amounts of water is accompanied by a pronounced decrease in the uric acid elimination. (This question is further discussed in a later paragraph.)

---

[1] "Practical Physiological Chemistry" (Hawk), Third Edition, p. 366.

TABLE I.—URIC ACID EXCRETION. EXPERIMENT I.

Day of experiment.	Number of sub-period.	Uric acid excretion.		Urine volume.	
		Sub-period	Total for day.	Sub-period.	Total for day.
		Preliminary Period (3 Days).			
		Gram.	Gram.	cc.	cc.
I			0.319		900
II			0.294		1330
III	1	0.049	0.267	140	1350
	2	0.044		235	
	3	0.074		260	
	4	0.028		360	
	5	0.072		355	
		Water Period (4 Days).			
IV	1	0.028	0.195	720	6720
	2	0.021		1750	
	3	0.033		1580	
	4	0.026		1360	
	5	0.087		1310	
V	1	0.037	0.131	680	6320
	2	0.016		1750	
	3	0.017		1400	
	4	0.040		1320	
	5	0.021		1170	
VI	1	0.016	0.150	730	6530
	2	0.062		1670	
	3	0.021		1200	
	4	0.024		1380	
	5	0.027		1550	
VII	1	0.019	0.148	620	5530
	2	0.036		1800	
	3	0.028		840	
	4	0.023		1300	
	5	0.042		970	
		Final Period (2 Days).			
VIII	1	0.046	0.212	140	1025
	2	0.036		185	
	3	0.034		170	
	4	0.033		215	
	5	0.063		315	
IX			0.279		790

A consideration of the uric acid output for the daily sub-periods of the first experiment fails to reveal any uniformity in the uric acid elimination for the different days. In some instances the maximum excretion occurred during the first $3^1/_2$-hour period, whereas on certain other days the second, third, or fourth sub-period, as the case may be, included the maximum yield. It is of interest that the largest urine flow was found to occur during the second sub-period on each day of the interval of high water ingestion. This uniformity did not hold for the preliminary or final periods. No relation was noted between the volumes of the urine fractions and their uric acid content.

TABLE II.—URIC ACID EXCRETION. EXPERIMENT II.

Day of experiment.	Urine data Uric acid content.	 Volume.	Water ingested.[1]
	Preliminary Period (3 Days).		
	Gram.	cc.	cc.
1	0.282	1090	500
2	0.267	997	500
3	0 274	770	500
	Water Period (2 Days).		
4	0 279	5250	5000
5	0 258	5800	5000
	Final Period (4 Days).		
6	0.261	1275	500
7	0 283	1160	500
8	0 254	1140	500
9	0 268	885	500

When we examine the data from the second experiment, as given in Table II, we find that the conditions during the interval of high water ingestion were entirely different from those which were observed in the similar period of the first study. The daily uric acid output for the preliminary period, however, was very similar to that already discussed in connection with the data from Experiment I. This logically follows from the fact that the subjects were of practically the same body weight and were being fed a very similar ration. The values for the period range from 0.267–0.282 gram per day. The initial day of the water period was accompanied by an increase of $4^1/_2$ liters in the water ingestion. Bearing in mind the uric acid findings of the first experiment, we would expect to observe an accompanying lowering of the uric acid output. However, the data indicate that no such decrease occurred in this case, inasmuch as the daily uric acid excretion for each day of the water period was an approximate duplication of those obtained during the low water ingestion of the preliminary period. When we pass to the final period with its normal water ration, we again fail to note any considerable or significant variation in the uric acid values.

Going no deeper into the question than a comparison of the analytical data obtained in the two experiments, it seems that copious water ingestion in the case of one subject caused a pronounced decrease in the daily output of uric acid, whereas in the case of the other subject similar experimental manipulation was productive of no alteration in the course of the uric acid elimination. With no other data at hand, then we would interpret the lack of uniformity observed as due to individuality. When we consider the known facts regarding the origin and excretion of uric acid, however, it is difficult to see how an increased water ingestion can be considered as a logical forerunner of a decreased uric acid excretion. To be sure, Genth[1] as far back as 1856 did obtain a lowered uric acid output after feeding a ration which embraced a comparatively high water intake. However, Genth used the Heintz method for the determination of his uric acid values, a method which is considered inaccurate. Later Schöndorf[2] using Salkowski's modification of Fokker's method secured data which indicated a slightly lowered excretion under the influence of high water ingestion.

---

[1] Exclusive of the water content of the milk.

On the other hand Laquer[3] and Schreiber[4] have each shown a slightly increased excretion of uric acid after feeding from 1–3 liters of water.

Recent tests made by us have indicated quite conclusively that the Folin-Shaffer procedure does not always yield the total uric acid output of urines which possess as low specific gravities as those obtained during the water periods of our experiments, *i. e.*, 1.003–1.010. For this reason we are not willing to interpret the data from our first experiment as indicating that copious water drinking has caused a decrease in the uric acid elimination, but are rather inclined to believe that a portion of the uric acid content of those urines of low density escaped determination by the Folin-Shaffer technic. It is possible that the factor of individuality has also exerted an influence, but we place more reliance upon the quantitative data obtained in our second experiment which show *no change* in the uric acid output under the influence of the ingestion of large volumes of water. We believe the data there set forth represent the true relations for this subject and that the urines were of such a character as to permit the securing of accurate data by means of the Folin-Shaffer procedure.[5] The values obtained for the water period of the first experiment we believe are too low and do not represent the absolute uric acid values for those days. Why the dilute urines from one subject should yield accurate data and similar urines from another subject should yield data apparently inaccurate when the same procedure was used in the two instances, we are unable to say. No interfering substances could be demonstrated to be present and it is rather difficult to see just how the urines from the two experiments could differ much in general characteristics, inasmuch as the dietary of each experiment was made up of the same constituents.

---

[1] Genth, Quoted by Schöndorf, *Arch. ges. Physiol.*, 46, 529.

[2] Schöndorf, *Arch. ges. Physiol.*, 46, 529.

[3] Laquer: Kongress für innere Medicin, 1896, p, 381.

[4] Schreiber, "Die Harnsäure," 1899, p, 38.

[5] It may be, of course, that the Folin-Shaffer method also failed to determin the total uric acid content of these urines. In that event an increased excretion of uric acid must have followed copious water drinking.

Summary.

Two experiments were made to demonstrate the influence of copious water drinking *between* meals upon the uric acid output. The subjects used were two young men 24 and 29 years of age respectively. Each experiment was divided into three periods, a preliminary period during which nitrogen equilibrium was established through the feeding of a uniform diet, a water period during which this uniform diet was supplemented by the daily drinking of a large volume of water *between* meals, and lastly a final period in which the dietary regimé of the preliminary interval was in force.

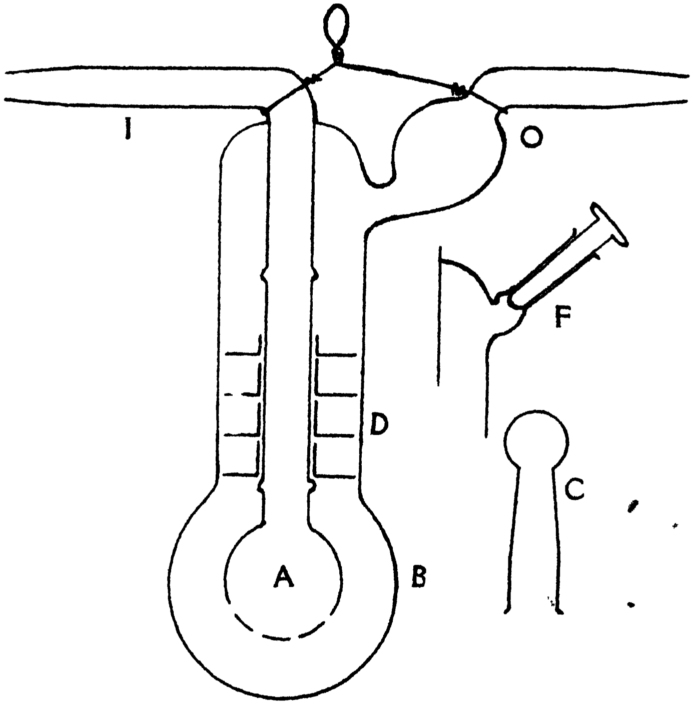
In one experiment copious water drinking caused no change in the uric acid output, whereas a pronounced decrease in this excretion was observed in the case of another subject. The data indicating a decreased elimination of uric acid under the influence of copious water drinking we believe to be due to the fact that the Folin-Shaffer procedure did not, in the case of this subject, determin the total uric acid content of those urines of extremely low density, *i. e.*, 1.003–1.010. This interpretation has been substantiated by tests made in another connection.

Upon those days when the urine for the twenty-four-hour interval was collected in five sub-periods, there was apparently no relation between the urine volume for the sub-period and the uric acid content. There was likewise no uniformity in the daily course of the uric acid excretion, the maximum output occurring on different days in the first, second, third, and fourth sub-periods respectively. The maximum urine flow occurred uniformly in the second sub-period of those days on which large volumes of water were being ingested. This uniformity was not observed on the days of low water ingestion.

URBANA, ILL.

NOTE.

A Convenient Potash Bulb.—More than a year ago the writer devised a potash bulb much like the one shown in the cut, and it proved to be so convenient and efficient that it was thought worth while to describe the no less efficient and much more convenient form shown. The cut is drawn to scale from one now in use. The inner and outer tubes, A and B, are made of very thin "condenser" tubing, the tubes I and O being of ordinary thickness. The essential feature is the disks, D, which fit so loosely between A and B that they can move freely up and down between the projections blown in the wall of A. The annular free spaces should be not less than 1 mm. broad. The disks are made by abruptly flaring glass tubing of proper bore and cutting off about 4 or 5 mm. from the end.



When gas is entering through I, it is first broken up into small bubbles on passing through the openings in A. (Instead of being blown into a bulb, the end of A may be flared to form a broad disk.) It is then trapped in succession by the disks which, when working properly, alternately rise and fall, continually wetting the walls of B with fresh solution. The lowest disk must not fall below the cylindrical part of B, and the uppermost must stop rising at least a centimeter below the outlet. The amount of liquid to be used depends on its viscosity and the rate of flow of the gas. Enough to just reach the second disk is usually sufficient. The cleanest way to introduce it is through the filling-tube, F, set on in a plane at right angles to that of I and O. The ground-in stopper is made of glass rod, and is rendered perfectly tight by means of stopcock grease.

In weighing, the caps, C, are placed on I and O, and the tube is suspended by means of a permanently attached loop of platinum wire, as shown.

This form of absorption bulb is less fragile than the Geissler bulb, has a much smaller surface and is considerably lighter. When filled it weighs from 35-40 grams. The method of filling obviates all danger of contact between the solution and the rubber connections. C. E. WATERS.

BUREAU OF STANDARDS, WASHINGTON,
September 29, 1910.

NEW BOOKS.

A Manual of Volumetric Analysis, Treating on the Subjects of Indicators, Test-papers, Alkalimetry, Including Assay of Drugs by Titration, Acidimetry, Analysis by Oxidation and Reduction, Iodimetry, Determinations by Precipitation, and by Color Comparison. By VIRGIL COBLENTZ, PH.D., Pharm. M, F.C S., Professor of Chemistry in the New York College of Pharmacy. Second edition, revised, completely reconstructed and enlarged by Anton Vorisek, Phar. D., Professor of Analytical Chemistry in the College of Pharmacy Columbia University, in the City of New York, with 37 illustrations. Philadelphia: P. Blakiston's Son & Co., 1012 Walnut Street. 1909.

"Denn was man schwarz auf weiss besitzt kann man getrost nach Hause tragen." While this suggestion was given by Mephisto to what was presumably a German student, the average American student does not have the time, or at least he thinks he has not the time to take notes for the purpose of taking them home. Neither is he content, as a rule, with such a large text as Sutton or Mohr that can be consulted in the departmental library. He is happiest when he has a textbook that does not contain much more than his immediate necessities demand.

This manual of volumetric analysis meets such a demand and meets its acceptably. Considerable information is crowded between the two covers.

In the first edition the ionic theory was applied to indicators only. In this the second edition it "has been extended to chemical reactions other than those of the indicators." Evidence of this extension is rather scarce in the text, being restricted mainly to a few pages in the chapter devoted to "Determinations by Neutralization."

"The didactic system (H = 1,000) of atomic weights used in the first edition has been dropped and replaced by the atomic weights of the International Committee of Atomic Weights. However, the rounded value of H = 1.01 for the official value 1.008 was adopted "to shorten long fractions and to facilitate calculations."

The book will, no doubt, continue to find many friends among students and teachers. EDWARD KREMERS.

History of Chemistry. By SIR EDWARD THORPE. Two volumes, 16mo., illustrated. Vol. 1, pp. xii + 195; Vol. 2, pp. vii + 202. New York: and London: G. P. Putnam's Sons. Price, cloth, 75 cents per volume.

These two volumes by the author of "Essays in Historical Chemistry" form a part of a series of books on the "History of the Sciences," the

"History of Astronomy" by George Forbes having previously appeared.

In the study of the natural sciences there is perhaps no part that is more commonly slighted or neglected than their history. Unfortunately this is still especially true of the history of chemistry. The study of the history of the development of the natural sciences is not only intensely interesting, but it offers rare opportunity to acquire breadth of view and culture, for the growth of scientific thought and methods is most intimately connected with the progress of mankind. No one can really fully appreciate what we know of chemistry without at least a rudimentary knowledge of the history of that science. But very few students of chemistry have read the monumental work of Kopp on the history of chemistry from cover to cover, indeed not many have read through the less comprehensive books like those of Ernst von Meyer or Ladenburg. Most students are so much engrossed with the work of mastering the science itself that they neglect its history, a study of which would not only clear up many difficult points, but would act as a source of inspiration for further vigorous efforts.

The present brief history of chemistry may be highly recommended to the student. It is written in a clear, interesting style, which can not fail to captivate the reader. The first volume traces the history from earliest times to the middle of the nineteenth century, and the second volume treats of the period from 1850 to the present day. The author presents the origin and growth of chemical views and theories as based upon experimental investigation. Considering the space allotted, he has succeeded very well on the whole, though to be sure it was necessary to greatly curtail many of the interesting phases of the history of the science. The volumes contain twenty-five portraits of noted chemists. Some of these have been printed for the first time. One of the special features of the volumes is that they contain many short biographical sketches of men prominent in the development of chemical ideas. In these sketches the author is at his best, as indeed one would expect from his "Essays in Historical Chemistry," which are classics. If any criticism is to be made on the books, it would be that these biographical sketches occupy too much space as compared with that devoted to the tracing of the development of chemical theories.

It is to be hoped that these volumes will stimulate renewed interest in the history of chemistry. May they act as an inspiration to the student of science and lead him to delve further into the more exhaustive treatises on chemical history, a study of which is indispensable to every one who really desires a thorough understanding of the chemical facts, laws, and theories that have thus far been accumulated.

The books are neatly bound in cloth, the paper is good and the print clear.
LOUIS KAHLENBERG.

Neuere Anschaungen auf dem Gebiete der anorganischen Chemie. By PROF. DR. A. WERNER. Second Edition Braunschweig. Friedrich Vieweg und Sohn. 1909. pp xv + 292. Price, 9 Marks; bound, 10 Marks

To the average chemist only a limited time is available for familiarizing himself with the details of developments in lines other than his own. The appearance of the first edition of this book in 1905 was therefore welcomed by all who had become interested in the remarkable work of Werner and his co-workers, yet who had gotten only a hazy idea of the subject, on account of the enormous mass of material appearing constantly in the journals. Since then the number of contributions to the literature has not grown less, rather has it increased. This has been due to the extension of the views developed from the study of the metal-ammonia compounds to the hydroxy compounds, basic salts, acids, bases, hydrolysis, dyestuffs, and the difficult but successfully exploited field of the polynuclear compounds. Consequently a new edition of the book has become necessary, and in this second edition the author has brought together in concise form, and with full bibliography, all of the later developments in this fascinating chapter of inorganic chemistry.

Based upon the experience gained from the first edition, the arrangement of the matter has been greatly improved, making the book much more readable to those unfamiliar with the subject.

The new edition shows clearly the development of the author's views concerning valence. His attitude from the outset has been that of one who puts forth no final solution of a problem, but rather a working hypothesis based upon a clear insight into relations among a mass of compounds hitherto considered inarticulate. His hypothesis of "secondary" or "auxiliary" valences has indicated the way for experimental work leading to the discovery of many new compounds, explained the constitution of many old ones, and demonstrated relations hitherto unrecognized. Doubtless, as the author himself believes, the final truth concerning these compounds has not yet been revealed; but certainly his views and work constitute a most important step toward that truth.

The diversified character of the developments in this complex subject can be understood only when it is known that the author, while possessing a fine scientific imagination, is also an indefatigable worker in the laboratory; that while interested primarily in inorganic, he is equally at home in physical and in organic chemistry.

It is to be hoped that at some early day Prof. Werner will publish a laboratory manual embracing the preparation of typical compounds in each important group, and especially the methods employed in passing from one group to another. Such laboratory directions exist, of course, in the literature, but they are so widely scattered that many turn aside from work in this field. The reviewer can imagine no more attractive subject for a student course in inorganic preparations than, for example, the cobaltammines, with their varying colors, their differences in ionization, and the multiplicity of possible transformations.

CHAS. H. HERTY.

Die Alkaloide. Eine Monographie der natuerlichen Basen. Von DR. ERNST WINTERSTEIN, Professor, und DR. GEORG TRIER, Assistant, an der eidgenössicschen polytechnischen Schule in Zurich. Verlag von Gebrüder Bronträger, Berlin, 1910.

The appearance of this book is very timely. While text-books on organic chemistry usually contain a short chapter on alkaloids, special treatises on this subject are few and appear at long intervals. The book is excellently gotten up from the standpoint of workmanship, and contains almost every alkaloid whose existence has been definitly established. By omitting detailed methods of manufacture, leaving out descriptions of alkaloidal salts, and cutting down bibliographic references to a minimum, the authors have managed to condense a vast subject into 340 pages. A special feature of the book is the special attention given to the physiological behavior of those alkaloids whose effect on living organisms has been tested. The book consists of a general introduction, a special part and a large chapter on the function and generation of organic bases in plants. The introduction consists of ten chapters: Definition; historical review; occurrence; general methods of preparation, detection and quantitative estimation; general properties; constitution and methods used for its determination; synthesis of alkaloids; physiological behavior; phytotoxins; relation between constitution and physiological action; classification. The authors distinguish between alkaloids in general and alkaloids proper. The first term applies to all nitrogenous bases found either in vegetable or animal organisms; the second is restricted to vegetable bases containing nitrogen in heterocyclic union and possessing physiological activity. In the chapter on physiological activity the supposition is advanced ascribing this activity to a molecular combination of alkaloid and protoplasm, the enormous effect of relatively small doses being due to the smallness of the molecular weight of the organic bases as compared with the exceptionally large molecular weight of the albumins. A thorough discussion is given of the remarkable tolerance of some animals towards poisonous bases, atropine, for example, having no effect upon the rabbit, and the lethal dose of morphine being ten times larger for chickens and a thousand times larger for goats than for man. The authors criticize the utility of antidotes whose action, like that of tannin, consists in the formation of insoluble combinations with the organic base. Since many alkaloids exist in the poisonous plants in the form of tannates, the administration of tannin cannot be expected to destroy the toxicity of the bases. In the chapter on the relation between constitution and physiological action, the authors, after enumerating the well-established regularities, arrive at the conclusion, expressed in the words of Schmiedeberg, that it will be more difficult to establish a scientific theory of this relation than of that between constitution and color. In the special part no attempt is made to classify the alkaloids according to any definit system. The aliphatic bases are treated first, then comes in succession the aromatic with an aliphatic side chain, pyridine, quinoline and isoquinoline derivatives, bases containing several nitrogen atoms in the molecule and finally the alkaloids of unknown constitution. In the voluminous chapter on the function and generation of alkaloids in the plants the authors review the various proposed theories, and express their preference for the supposition that the vegetable bases are catabolic products of the albumins, and that their formation has no other purpose than the removal of nitrogenous decomposition products that have become useless or even harmful to the living plant. Pictet's general theory of the formation of the alkaloids from certain so-called protoalkaloids of simple constitution which are themselves decomposition products of the albumins is accepted in its general features, but it is shown that, contrary to that theory, formaldehyde cannot be regarded as the direct methylating agent, and that Pictet's scheme of the formation of alkaloids with a pyridine nucleus from pyrrole is not quite satisfactory. The objection to formaldehyde as a direct methylating agent is based, among other considerations, upon the fact established by Winterstein that alkaloids are frequently formed in seeds during germination in the dark when there is no photosynthesis to produce formaldehyde. The authors think that the direct methylating agent is methyl alcohol which, however, may in some cases owe its formation to the aldehyde produced primarily. The alkaloids containing a pyridine nucleus are formed not from pyrrole, but from lysine produced in the splitting up of the albumins. Even the nitrogen-free groups, like benzoyl, cinnamyl, etc., frequently present in the molecule of alkaloids, are produced from the amino acids of the albumins by a reaction similar to the one called by Ehrlich "alcoholic fermentation of amino acids." An important role in the formation of alkaloids is ascribed to the betaines the constitution of which is assigned to several bases, *e. g.*, guvacine and arecaine, which hitherto were not supposed to be betaines. The authors' views are illustrated by many examples showing the genetic relations between the albumins and the alkaloids. A characteristic feature of the successive phases of the transformation of the former into the latter consists in the destruction ("blocading") of the reactivity of the hydrogen atoms of the amino groups by reactions of methylation or, in some cases, condensations with alcohols, phenols or aldehydes. For this reason the authors propose a new definition of alkaloids as "organic compounds produced in the formation or transformation of protoplasmic substances (proteins, proteids, phosphatides, etc.) in such a way that the reactive hydrogen atoms of the basic groups are closed, so that the resulting products are unable to regenerate the original or to form new protoplasmic substances." The presence of choline and of purine bases in the molecules of the albumins is ascribed to the action of ammonia on some of the nitrogen-free intermediate products of photosynthesis. The book is full of suggestions and deserves a prominent place in every well-equipped library. H. M. GORDIN.

RECENT PUBLICATIONS.

Annual Report of His Majesty's Inspectors of Explosives. London: Wyman and Sons.

BENDER, T.: **Der praktische Hochofenbetrieb.** Halle a/S. 5.40 M.

BLOCHMANN, R.: **Anleitung zur Darstellung chemischer anorganischer Präparate.** Leipzig· Veit & Co. 2 Aufl. 8°, 2.50 M.

BOMBICI, L.: **Mineralogia descrittiva.** Third edition. Mailand: U. Hoepli, 16°, 300 pp., 3 L.

CHAPLET, A., AND ROUSSET, H.: **Les succédanés de la soie.** (*a*) Les soies artificielles. (*b*) Le mercerisage et les machines à merceriser. Paris· Masson et cie, Preis je 2.50 Fr.

DILLING, W. J.: **Atlas der Krystallformen und der Absorptionsbänder der Hämochromogene.** Stuttgart: 4°, 28 M.

ESCALES, R.: **Chloratsprengstoffe.** Leipzig: Veit & Co. 8°, 8 M.

EXNER, F.: **Ueber Radiumforschung.** Wien: 8°, 24 pp., 7 M.

FRIEDRICH, K.· **Mitteilungen aus dem Institut für Metallographie und Probierkunde an der kgl. sächs. Bergakademie Freiberg.** Heft: 1 Halle a/S, 12 M.

GRUND, G.· **Organanalytische Untersuchungen über den Stickstoff u. Phosphorstoffwechsel u. ihre gegenseitigen Beziehungen.** Halle: 8°, 83 pp.

Handbuch der Biochemie des Menschen und der Tiere. Herausgegeben von C. Oppenheimer. 25 Lieferung. Jena, 8°, Jede Lieferung. Jena 8°, Jede Lieferung 5 M.

HOLLEMAN, A. F.: **Lehrbuch der anorganischen Chemie.** 8 Aufl. Leipzig: 8°, 568 pp., 10 M.

HENGLEIN, M.: **Lötrohrprobierkunde.** Qualitative Analyse mit Hilfe des Lötrohres. Leipzig: 12°, 83 pp., 0.80 M.

HERZ, W.: **Sammlung chemischer und chemisch-technischer Vorträge.** Stuttgart: 8°, 6 M.

HOOD, G. F.: **A First Year's Course of Inorganic Chemistry.** London: Rivingtons.

International Catalogue of Scientific Literature. Published by the Royal Society of London. 8°, 1145 pp., 37.50 M.

Jahresbericht über die Untersuchungen und Fortschritte auf dem Gesamtgebiete der Zuckerfabrikation. Begr. v. K. Stammer. Braunschweig: F. Vieweg & Sohn. 361 pp., 16 M.

KAYSER, H.: **Handbuch der Spektroskopie.** Leipzig: 8°, 853 pp., 48 M.

KIRK, E.: **The Cupola Furnace.** Third edition. Philadelphia: Baird, 8°, 459 pp., $3.50.

KREMANN, R.: **Leitfaden der graphischen Chemie. Erläuterung einiger wichtiger Schulbeispiele.** Berlin: 8°, 36 pp., 6.60 M.

LENARD, P.: **Ueber Aether und Materie.** Heidelberg: C. Winters, 1.20 M.

LIPSKI, J.: **Ueber Synthese des Ammoniaks aus den Elementen.** Braunschweig: 8°, 57 pp., 1.80 M.

MASSELON, ROBERTS AND CILLARD: **Le Celluloid, Fabrikation, Applications, Substituts.** Paris: A. D. Cillard, 20 Fr.

MICHEL, F.: **Ueber die Reaktion zwischen Sulfurylchlorid und Ammoniak.** Grüningen· J. Wirz, 8°.

MOUREU, C.: **Notions fondamentals de chimie organique.** Third edition. Paris: Gauthier-Villars.

PRESCHER AND RABS: **Bakteriologisch-chemisches Praktikum.** 2 Aufl. Würzburg: A. Stuber, 6 30 M.

RAUTER, G.: **Allgemeine chemische Technologie.** 2 Aufl. Leipzig: 12°, 148 pp., 8 M.

RIEKE, R.: **Das Porzellan.** Hannover: 8°, 201 pp., 4.60 M.

RÜDISÜLE, A.: **Die Untersuchungsmethoden des Eisens und Stahls.** Berlin: 11 M.

SCHWALBE, C. G.: **Die Chemie der Cellulose, unter besonderer Berücksichtigung der Textil-u. Zellstoffindustrien.** Berlin: 8°, 1 Hälfter, pp. 1–272, 9.60 M

SEAMON, W. H.· **A Manual for Assayers and Chemists.** New York: Wiley, 8°, 255 pp, $2.50.

SIDERSKY, D.: **La réfractométrie et ses applications pratiques.** Paris: Masson & Cie, 172 pp., 3 Fr.

SILBERBERG, L.: **Gesetz über Absatz von Kalisalzen vom 23 Mai 1910.** Halle a/S: 5.40 M.

STANGE, A.: **Illustr. Jahrbuch der Wirtschaft und Technik im deutschen Kalisalzbergbau, nebst Reichskaligesetz mit einer krit. Einleitung.** Berlin: Montan-Verlag, 20 M.

STILLMAN, T.: **Engineering Chemistry.** A Manual of Quantitative Chemical Analysis for the use of Students, Chemists and Engineers. Easton, Pa. Chemical Pub. Co. 8°, 744 pp, $5.00.

STROHMER, F.: **Ueber das Vorkommen von Raffinose in Rohzucker und deren Bestimmung:** Wien.

TILDEN, SIR WM. A.: **The Elements.** New York: Harper and Brothers.

TOWNSEND, C. F.: **Chemistry for Photographers.** Routledge: Fifth edition, 8°, 129 pp., 1 s.

VERMOREL, V., AND DANTONY, E.: **Utilisation des sous-produits de la vigne et du vin. Paris:** L. Laveur, 8°, 4 Fr.

WALDEN, R.: **Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge** (Sammlung chemischer und chemischtechnischer Vorträge, herausgegeben von W. Herz. Band 15, Heften 8–12, pp. 287–471). Stuttgart: 8°, 6 M. Preis für den getzt voll, ständigen Band, 471 pp., 12 M.

WILLIAMS, R.: **Essentials of Chemistry**; experimental, descriptive, and theoretical. Boston: Ginn, 421 pp., $1.25.

ZERR, G., AND RUBENKAMP, R.: **Handbuch der Fabrikation.** Second edition. Berlin. Union Deutsche Verlagsgesellschaft, 30 M.

Index to Volume XXXII, 1910

ABBOTT, G. A. Rate of hydration of pyrophosphoric acid A correction.................. 1576

ABDERHALDEN, E. Fortschritte der naturwissenschaftlichen Forschung (book), 1362, Handbuch der biochemischen Arbeitsmethoden (book).................................. 726, 895

ABEGG, R. and AUERBACH, F. Handbuch der anorganischen Chemie in 4 Bänden (book)...... 247

ABEL, R Bakteriologisches Taschenbuch, enthaltend die wichtigsten technischen Vorschriften zur bakteriologischen Laboratoriumsarbeit (book)...................... 247

4-Acetaminoacetanthranil, 1299, quinazolones from............................ 1301

5-Acetaminoacetanthranil, 1301, quinazolones from, 1311; the synthesis of 6- and 7-amino-2-methyl-4-quinazolones from 4- and 5-acetaminoacetanthranils..................... 1297

p-Acetaminobenzamide, preparation.............................. 1496

p Acetaminobenzonitrile, preparation.............................. 1496

6 Acetamino-2,3-dimethyl-4-quinazolone.............................. 1311

7-Acetamino-2,3-dimethyl-4-quinazolone.............................. 1305

6-Acetamino-2-methyl-3-amino-4-quinazolone.............................. 1312

7-Acetamino-2-methyl-3-amino-4-quinazolone, 1308, 1310, hydrochloride.............. 1308

7-Acetamino-2-methyl-3-*p*-anisyl-4-quinazolone.............................. 1307

6-Acetamino-2 methyl-3-ethyl-4-quinazolone.............................. 1312

7-Acetamino 2 methyl-3-ethyl-4-quinazolone.............................. 1306

7-Acetamino-2-methyl-4-hydroxyquinazoline.............................. 1301

7-Acetamino-2-methyl-3-isoamyl-4-quinazolone.............................. 1307

7 Acetamino-2-methyl-3 *α*-naphthyl-4-quinazolone.............................. 1308

7 Acetamino 2-methyl-3-*p*-phenetyl-4-quinazolone.............................. 1307

6-Acetamino-2-methyl-3-phenyl-4-quinazolone.............................. 1312

7-Acetamino-2-methyl 3 phenyl-4-quinazolone.............................. 1307

6-Acetamino-2 methyl 3-*n* propyl-4-quinazolone.............................. 1312

7 Acetamino-2-methyl-3-*n*-propyl-4-quinazolone.............................. 1306

7-Acetamino-2-methyl-4-quinazolone.............................. 1301

7 Acetamino-2 methyl 3 7′-[2′-methyl-4′-quinazolone]-4-quinazolone.............................. 1311

Acetic acid, equivalent conductance of, 163, ionization of, 164; surface energy of.......... 1169

Aceto-2-acetyl-4-aminonaphthol 1 and properties.............................. 1481

Acetoanthranilic acetohydrazide.............................. 1659

7-Acetoxy-2-methyl-4-quinazolone.............................. 1305

7-Acetyl-4-benzylidenaminonaphthol-1 and properties.............................. 1482

2-Acetyl-4-cinnamylidenaminonaphthol-1 and properties.............................. 1483

Acetylmethyl *p* nitrophenylethylamine.............................. 767

Acetylmethylphenylethylamine.............................. 767

2-Acetyl-naphthol-1, some derivatives of.............................. 1477

2-Acetyl-4-piperonylidenaminonaphthol and properties.............................. 1482

Acid, $C_9H_{12}O_4$, and barium salt, 1666, $C_5H_8O_2N\ CO_2H$, 1668, and barium salt, 1669, new monocarboxylic in the pumpkin seed.............................. 354

Acid amide, $C_8H_{11}O_2CONH_2$, 1666, $C_5H_8O_2NCONH_2$, formation of.............................. 1668

Acidity, estimation of intensity of, with dinitrohydroquinone.............................. 687

Acids, adiabatic determination of heats of solution of metals in, 431, 1176; destruction of invertase by, 985, influence of, on the activity of invertase, 774, 1220, of the phenylpropiolic series and their condensation to naphthalene derivatives, 212, rearrangements of unsaturated, 1339, the heat of solution of metals in concentrated, 452; titration of.............................. 829ff

Acid value, determination of, of crude fat and its application in the detection of aged foods.............................. 568

ACKERMANN, E Dictionary of Portuguese Mining Terms, with French, English, and German Equivalents (book).............................. 1110

ADAMS, W Hints on Amalgamation and the General Care of Gold Mills (book).......... 575

Adsorption of air by silver phosphates.............................. 315

Aeration, quantitative distillation of ammonia by.............................. 689

Agricultural and Food Chemistry, division of..............................Pr. 25, 103, 121

Agriculture, Handbuch der landwirtschaftlichen Bakteriologie (Löhnis, book)............ 1108

Albe, E. E. The Electron Theory (book).............................. 1362

Alcohol, effect on invertase, 1350; equilibrium in the system. potassium iodide, iodine and aqueous alcohol, 1367; isolation of a new dihydric.............................. 89

Alcohol, absolute, apparatus for ... 698
Alcoholates, pseudoammonium bases and their ... 1279
Aldehydes, aromatic, the salts of bases formed by condensing *m*-aminodimethylaniline and *m*-aminodiethylaniline with ... 382
ALEXANDER, J. Some colloid-chemical aspects of digestion, with ultramicroscopic observations 680
Alkali amalgams ... 622
Alkali earth amalgams ... 622
Alkalies, destruction of invertase by, 985; influence of, on the activity of invertase ... 774, 1220
Alkalinity, estimation of intensity of, with dinitrohydroquinone ... 687
Alkaloids, application of the Volhard method to the estimation of, 132; Die Alkaloide. Eine Monographie der natuerlichen Basen (Winterstein, Trier, book) ... 1696
Alkylations with dimethyl sulphate ... 761
ALLEN, A. H. Commercial Organic Analysis (book) ... 726
ALLEN, E. T. and Johnston, J. The exact determination of sulphur in soluble sulphates ... 588
Alloxan, instability of ... 809, 1362
Alloys of cadmium, bismuth and lead ... 1390
ALSBERG, C. L. Recent work in biological chemistry (review) ... 704
ALTMAYER, V. Ueber das Methangleichgewicht, die Beziehungen zwischen Nickel und Wasserstoff und einige Methansynthesen mit Calciumhydrür (book) ... 726
Alums, diffusion phenomena of ... 1378
Amalgam, alkali and alkali earth, 622; the interaction of mixed salt solutions and liquid ... 502
AMEND, C. G. See Bogert, M T.
American Chemical Society, Board of Directors, Pr. 2, 44, 95, 121; Boston Meeting, Pr. 30; Council, Pr. 1, 30, 51, 63, 77, 83, 89, 95, 105, 121, 125; Forty-first general meeting, minutes, Pr. 9; Forty-second general meeting, minutes, Pr. 99; report of the editor of the Journal, Pr. 15; report of the Finance Committee for the year 1909, Pr. 21; report of the Journal of Industrial and Engineering Chemistry for the year 1909, Pr. 17; report of the Librarian for the year 1909, Pr. 22; report of the Paper Committee of the American Chemical Society, Pr 32, report of the Secretary for 1909, Pr. 11; report of the Treasurer, Pr. 19; Resolutions governing committees, Pr. 106; San Francisco Meeting ... Pr. 62, 88
Amines, action of, on phthalic acid, 113, 1319; condensation of some primary aromatic, with chloralaniline, 973; researches on ... 761
Amino acids, fate of, in the organism ... 671
p-Aminobenzonitrile, some derivatives of ... 1494
m-Aminodiethylaniline, derivatives of, 386, the salts of bases formed by condensing *m*-aminodimethylaniline and, with aromatic aldehydes ... 382
m-Aminodimethylaniline, the salts of bases formed by condensing *m*-aminodiethylaniline and, with aromatic aldehydes ... 382
7-Amino-2,3-dimethyl-4-quinazolone ... 1306
Aminoisocampholactone ... 1667
6-Amino-2-methyl-4-quinazolone ... 1311
7-Amino-2-methyl-4-quinazolone, and derivatives ... 1301
6-Amino-2-methyl-4-quinazolones, synthesis of ... 1297
7-Amino-2-methyl-4-quinazolones, synthesis of ... 1297
m-Aminophenol, condensation products of mellitic acid with ... 189
Ammonia, quantitative distillation of, by aeration ... 689
Ammonia, solid hydrates of ... 748
Ammonia nitrogen, determination of, in water in the presence of hydrogen sulphide ... 1256
Ammonium acetate, conductance of solutions at 18, 100 and 156°, 165; solutions at 18, 218 and 306° ... 171
Ammonium acetate, hydrolysis of, at 100 and 156°, 168; at 218 and 306° 172, high temperatures. 159
Ammonium aluminium alum, diffusion of ... 1381, 1383
Ammonium chloride, a dynamic method for measuring vapor pressures, with its application to benzene and, 1448, 1453, 1457; equivalent conductance of, 161; reaction between potassium dichromate and, when heated ... 178
Ammonium chrome alum, diffusion of ... 1380, 1381, 1382
Ammonium ferric arsenate ... 628
Ammonium hydroxide, equivalent conductance of, 163; ionization of ... 164
Amylase, pancreatic study of the action of ... 1087
Amylases, studies on ... 1073, 1089
Analyses of some Greek vases ... 1257
Analysis, A Manual of Qualitative Analysis (McGregory, book), 243; an application of the Folin method to the determination of the ammoniacal nitrogen in meat, 561; An Introduction

to Chemical Analysis for Students of Medicine, Pharmacy and Dentistry (Rockwood, book), 243; application of the Volhard method to the estimation of alkaloids, 132; conditions affecting the electrolytic determination of copper, 1264; determination of ammonia nitrogen in water in the presence of hydrogen sulphide, 1256; determination of iodine in protein combinations, 692; determination of the acid value of crude fat and its application in the detection of aged foods, 568; determination of total sulphur in organic matter, 977; electric combustion furnace for methane determination, 949; electrolytic determination of chlorine in hydrochloric acid with the use of a silver anode and a mercury cathode, 1468; exact determination of sulphur in soluble sulphates, 588; influence of chlorine upon the determination of nitric nitrogen, 756; of calcium bromide, 1577; of tin-antimony alloys, 1241; progress in systematic qualitative organic, 1049; Quantitative Chemical Analysis· Adopted for Use in the Laboratories of Colleges and Schools (Clowes, Coleman, book), 244; quantitative determination of arsenic, 518, 520; quantitative distillation of ammonia by aeration, 689; rapid and accurate method for the determination of titanium, 957, resolutions governing committees of the American Chemical Society, and of its divisions, having to do with the standardization of methods of, Pr. 106; speedy detection of potassium in small amounts, 78; the phenolsulphonic acid method for the determination of nitrates in water, 630; the rapid determination of copper, silver, cadmium and bismuth by means of the mercury cathode and stationary anode, 1231, Treatise on Qualitative Analysis (Sellers, book), 242, use of organic electrolytes in separating cadmium, 1251, colorimetric, determination of manganese in the presence of iron, 965; elementary, by means of a calorimetric bomb, 547; volumetric, a source of error in permanganate titrations; preliminary note, 1204, A Manual of (Coblentz, book), 1693, Manual théorique et pratique d'analyse volumétrique (Duparc, Basadonna, book), 812; method of determining iodide in the presence of chloride, bromide, or free iodine, 1193, new method for cobalt and nickel, 757, new method for the determination of manganese, 1250, of cerium in cerite and monazite, 642; quantitative application of the theory of indicators to, 815; titration of ferrous salts in the presence of hydrochloric and phosphoric acids 539

Anderson, F. Hilfsbuch für Warme und Kälteschutz (book).................. 1362

Andouard, A Nouveaux éléments de pharmacie (book)...................... 1536

Andrés L. E Der Kesselstein, Seine Entstehung und Verhütung (book).............. 1110

Aniline, condensation of, with chloral-aniline 974

3-Anilino-4-quinazolone-2-carboxylic acid, ethyl ester.......................... 126

Anisolation..194

Anisylidene-*m*-aminodimethylaniline 386

Annuals, Annuaire pour l'An 1910 (book)...................................... 144

Anode, electrolytic determination of chlorine in hydrochloric acid with the use of a silver anode and a mercury cathode, 1468; rapid determination of copper, etc , by means of the mercury cathode and stationary anode, 1231, rapid determinations and separations by means of the mercury cathode and stationary anode.. 1628

Anselmino, O Das Wasser Experimentalvorträge (book).............................. 1362

Anthranilic acid, bromination of.. 770

Antimony alloys, analysis of tin-antimony alloys 1241

Apparatus, a convenient potash bulb, 1691, an adiabatic calorimeter for use with the calorimetric bomb, 461, 464, an adjustable automatic burette, 703; an improved siphon, 810; calorimetric bomb, 550, electrolyzing tube used in determining the atomic weight of mercury, 1123; extraction, 1533, for absolute alcohol, 698, for determining atomic weight of vanadium, 1605; for determining heats of combustion, 271; for determining heats of solution of metals in acids, 442, for determining molecular weights by vapor pressure lowering, 1616; for determining potential of the sodium electrode, 1461, 1464, 1465; for determining solubilities at high temperatures, 51; for determining vapor pressures, and boiling points of, 907; for determining vapor pressures of solids and liquids, 1419; for drying flasks, etc , 650; for estimation of small quantities of nitrogen by Pelouze reaction, 1239; for measurement of vapor densities of easily volatil substances, 1624; for preparation of tantalum chloride, 1129; for preventing loss of drops, 446, for the determination of arsenic, 520, 962; for transference experiments with thallous sulphate and lead nitrate, 1556; modified buret for standard alkali solutions (note), 971; new normal solution and reagent bottle, 1277; rack for holding reagents in bulk, 884; red lines for a balance scale 884

Arendt, R. Grundzüge der Chemie und Mineralogie (book).............................. 1110

Arrhenius, S. Lehrbuch der Elektrochemie (book).................................. 1008

Arlt, F R. v. Laboratoriumsbuch für die Zementindustrie (book)........................ 1362

Armitage, F. P. A History of Chemistry (book).................................. 428

Armstrong, E. F. The Simple Carbohydrates and the Glucosides (book), review 725, title 813

Arrhenius, S. Die Atmosphäre der Planeten (book), 1363; Theorien der Chemie. Uebersetzt von Alexis Finkelstein (book).. 247

Arsenates, some new double 626

Arsenic, apparatus for the determination of, 962; atomic weight of, 2, 260; effect of the presence of, in the electrolytic determination of copper, 1275; quantitative determination of, 518, 520; retention of, by iron and other metals 519, 522

Arthus, M. Elemente der physiologischen Chemie (book), 1536; Précis de chimie physiologique (book) 1008

Ashley, H. The Colloid Matter of Clay and its Measurement (book) 1110

Askenasy, P. Einführung in die technische Elektrochemie (book) 1110

Asparagine, influence of, upon the diastatic power of amylases 1103

Atkins, K. N. See Renshaw, R. R.

Atom, Le Cinquantenaire de l'atomecanique ou de la Mécanique des atomes (Hinrichs, book) 812

Atomic weight, of calcium, 1577, of hydrogen, 513, of mercury, 1117, of phosphorus, 298; of tantalum, 1127, of vanadium, 1603; annual report of the international committee on, 1113, Experimentelle Untersuchungen über Atomgewichte (Richards, book), 242; history of the revisions of the, of lithium, 10, of silver and iodine, 1591, of silver, lithium and chlorine, 4; report of international committee on, 1, seventeenth annual report of the committee on, determinations published during 1909 255

Auerbach, F. See Abegg, R.

Aufhäuser. Vorlesungen über Brennstoffkunde (book) 894

Aulard, A. See Vrancken, E.

Austin, L. S. The Metallurgy of Common Metals, Gold, Silver, Iron, Copper, Lead and Zinc (book) 428

Autenrieth, W. Die Auffindung der Gifte und stark wirkender Arzneistoffe (book) 247

Azobenzenes, the stereomeric 1294

Bactericidal properties of lecithins and choline salts 130

Bacteriology, Handbuch der landwirtschaftlichen Bakteriologie (Löhnis, book), 1108, Outline of Bacteriology (Ellis, book) 726

Bagshaw, W Elementary Photomicrography (book) 247

Bailey, C. H. First Stage Inorganic Chemistry (Theoretical) (book) 247

Baird, H. C The Practical Dry Cleaner, Scourer and Garment Dyer (book) 247

Balance scale, red lines for 884

Balke, C. W. The atomic weight of tantalum 1127

Bancroft, W D Division of Physical and Inorganic Chemistry (report) .... Pr 23

Barium hydroxide, solubility of barium nitrate and, in the presence of each other 1383

Barium nitrate, solubility of barium hydroxide and, in the presence of each other 1383

Barium sulphate, conductance of saturated solutions, 53; effect of nitrates on the precipitation of, 613; occlusion of sulphuric acid and sulphates by, 592, 603, 608, solubility of, at high temperatures 50

Barker, G. F. (obituary of) .... Pr 113

Barlow, W E. The binary and ternary alloys of cadmium, bismuth and lead 1390

Barneby, O. L and Isham, R. M. A rapid and accurate method for the determination of titanium 957

Barthel, C. Methods Used in the Examination of Milk and Dairy Products (book) 1110

Bartow, E. and Harrison, B. H. Determination of ammonia nitrogen in water in the presence of hydrogen sulphide 1256

Barus, C. Condensation of Vapor as Induced by Nuclei and Ions (book) 1363

Basadonna, M. See Duparc, L.

Bases, colored salts of Schiff's, 382; ether thioureas and their relation to pseudoammonium bases, 1279; titration of .... 829ff.

Basic properties of oxygen compounds with bromine and iodine 1330

Baskerville, C General Inorganic Chemistry (book), review 240, title 726

Baskerville, C. and Curtis, R. W. Laboratory Exercises in Inorganic Chemistry (book) .. 727

Baskerville, C. and Stevenson, R. Apparatus for drying flasks, etc 650

Bates, S J. See Tingle, J. B.

Battegay, A. Conférences de pharmacie, Tome 4. Analyses d'urines, de fèces, de lait (book). 895

Battelli, A., Occhialini, A., and Chella, S. Die Radioaktivität (book) 1008

Bauckner, J. Chemische Grundgesetze u. Grundbegriffe, berarbeitet durch Schüllerübungen (book) 1008

Baud, E. Industries des acides minéraux. Acides sulfurique, chlorhydrique et azotique (book) 894

Bauer, A. Zur Geschichte des Tellurs (book) 1363

Bauriedel, F Untersuchung über das Platin Hexabromoplatineate organischer Ammoniumbasen (book) 1363

Bausor, H. W. First Stage Inorganic Chemistry (Practical) (book) 247

Baxter, G. P. A revision of the atomic weight of silver and iodine, 1591; see Richards, T.W.

Baxter, G. P. and Jones, G. A revision of the atomic weight of phosphorus 298
Bayliss, W. M. Das Wesen der Enzymwirkung (book) 1536
Beal, G. D. See Bogert, M. T.
Beckurts, H. Die Methoden der Massanalyse (book) 1110
Behre, P Ueber einige Adsorptionserscheinungen (book) 247
Bell, J. M. The rate of extraction of plant food constituents from the phosphates of calcium and from a loam soil, 879; see Cameron, F. K
Bender, T. Der praktische Hochofenbetrieb (book) 1698
Benedict, F G and Higgins, H. L. An adiabatic calorimeter for use with the calorimetric bomb 461
Benner, R C. The rapid determination of copper, silver, cadmium and bismuth by means of the mercury cathode and stationary anode 1231
Benner, R C and Hartmann, M L Rapid determinations and separations by means of the mercury cathode and stationary anode 1628
Bennett, H. G The Manufacture of Leather (book), 247, see Smith, G. McP
Benolt, F. La néo métallurgie, ses moyens et ses methodes (book) 1537
Benthaus, W Ueber braunes amorphes Silicium (book) 1363
2-Benzalacetyl-4-nitronaphthol 1 and properties 1483
Benzene, a dynamic method for measuring vapor pressures, 1448, 1451, 1452, heat of combustion of, 280, surface energy of 1167
Benzene ring, Die orientierenden Einflusse und der Benzolkern (Obermiller, book) 251
p-Benzenesulphonaminobenzonitrile, preparation 1498
Benzidylcamphoformenamine 1505, 1516
Benzidylcamphoformenaminecarboxylic acid 1515
p-Benzoylaminobenzonitrile, preparation 1497
1-Benzoylphenyl-3-methyl-5-pyrazolone, 1489, 1490, hydrochloride 1491
Benzylidene-*m* aminodimethylaniline 385
Berdel, E Einfaches chemisches Praktikum fur Keramiker, Glastechniker, Metalltechniker usw. (book) 428
Berl, E See Lunge, G
Berlin, P Die Bayerische Spiegelglasindustrie (book) 1363
Bersch, W Hefen, Schimmelpilze und Bakterien (book) 1363
Bertelsmann, W Rechentafeln fur Beleuchtungstechniker (book) 813
Berthelot, und Saint-Giles, P de Untersuchungen über die Affinitäten Ueber Bildung und Zersetzung der Aether (book) 1008
Berthier, A L'éclairage industriel (book) 1537
Bertlaux, L See Hollard, A.
Bertrand, G and Thomas, P Guide pour les manipulations de chimie biologique (book) 1537
Betts, A G Bleiraffination durch Elektrolyse (book) 1363
Bibliography of phenylether and its derivatives 1293
Biedermann Die Sprengstoffe, ihrer Chemie und Technologie (book) 1110
Biedermann, R. Chemiker-Kalendar 1910 Hilfsbuch fur Chemiker, Physiker, Mineralogen, Industrielle, Pharmazeuten, Huttenmänner (book) 727
Biltz, H Qualitative Analyse anorganischer Substanzen (book) 247
Binz, A. Chemisches Praktikum für Anfanger (book), 247, Kohle und Eisen. Aus Wissenschaft und Bildung Einzeldarstellung aus allen Gebieten des Wissens (book), 575, Ursprung und Entwicklungen der chemischen Industrie (book) 1008
Biochemistry of nucleic acids 231
Biological chemistry, section of .... Pr 28
Birckenbach, L. Die Untersuchungsmethoden des Wasserstoffperoxyds (book) 248
Birnbaum, K Leitfaden der chem Analyse (book) 248
Bismuth, rapid determination of, by means of the mercury cathode and stationary anode 1231
Bismuth alloys, binary and ternary alloys of cadmium, lead and bismuth 1390
Bitumen, grahamite, a solid native 1032
Blanchard, A. A Synthetic Inorganic Chemistry (book) 1008
Blanchard, W. M Laboratory Exercises in General Chemistry (book), review 1109
Blasdale, W. C and Cruess, W. Conditions affecting the electrolytic determination of copper 1264
Blochmann, R Anleitung zur Darstellung chemischer anorganischer Präparate (book) 1678
Blouet, M. Nouvelles manipulations de chimie (book) 1537
Blowpipe analysis, Elements of Mineralogy, Crystallography and Blowpipe Analysis (Moses, Parsons, book) 144
Böhm, C. R. Die Fabrikation der Glühkörper für Gasgluhlicht (book) 813
Bogert, M. T. A review of some recent investigations in the quinazoline group, 784, the instability of alloxan (note) 809

Bogert, M. T., Amend, C. G. and Chambers, V. J. Researches on quinazolines (XXV). The synthesis of 6- and 7- amino-2-methyl-4-quinazolones from 4- and 5-acetaminoacetanthranils 1297

Bogert, M. T., Beal, G. D. and Amend, C. G. Researches on quinazolines (XXVI). The synthesis of some stilbazoles, hydrazones and Schiff bases in the 4-quinazolone group.. 1654

Bogert, M T. and Gortner, R. A. Researches on quinazolines (XXIV). On oxalyl anthranilic compounds and quinazolines derived therefrom.................. 119

Bogert, M. T. and Wise, L. E. Some derivatives of *p*-aminobenzonitrile.................. 1494

Boiling point, equation, 667; of mercury.................. 1446

Boiling points, common thermometric error in the determination of, under reduced pressure, 905; determination of, under constant conditions of even minute quantities of liquids and of non-fusing solids.................. 897

Bollenbach, H. Laboratoriumsbuch für die Tonindustrie (book), 1537; Neue Massanalytische Methoden zur Bestimmung von Eisen und Blei (book).................. 1537

Boltzmann, L. Vorlesung über Gastheorie. (2 Teile) Teil I: Theorie der Gase mit einatomigen Molekülen, deren Dimensionen gegen der mittlere Weglänge verschwinden. 2, unveränderter Abdruck (book).................. 895

Bomb, calorimetric, an adiabatic calorimeter for use with the, 461; elementary analysis by means of a.................. 547

Bombici, L. Mineralogia descrittiva (book).................. 1698

Bornemann, G. Stöichiometrie (book).................. 248

Bornemann, K. Die binären Metallegierungen (book).................. 248

Bothas, L. Massendestillation von Wasser (book).................. 248

Bottler, M. Modern Bleaching Agents and Detergents (book).................. 727

Bottomley, S. E. Photography in Principle and Practice (book).................. 428

Bouchonnet, A. Industries du plomb et du mercure. Bd. I. Metallurgie (book).................. 575

Bourquelot, E. Le Centenaire du Journal de Pharmacie et de Chemie (book).................. 1008

Bowsen, L. T. The speedy detection of potassium in small amounts (note).................. 78

Bray, W. C. A source of error in permanganate titrations; preliminary note, 1204, the hydrolysis of iodine and of bromine.................. 932

Bray, W. C. and MacKay, G. M. J. A volumetric method of determining iodide in the presence of chloride bromide, or free iodine, 1193, the conductance and ionization of potassium tri iodide, and the equilibrium between iodine, iodide, and polyiodides in aqueous solution, 914; the equilibrium between solid cuprous iodide and aqueous solutions containing cupric salt and iodine.................. 1207

Breckenridge, J. E. Division of Fertilizer Chemistry (report)..................Pr 25

Brenton, B. F. P. See Tingle, J. B.

Brochet, A. La soude électrolytique (book).................. 1363

Bromic acid, reaction between hydriodic acid and, in presence of much hydrochloric acid.... 644

Bromide, volumetric method of determining iodide in the presence of chloride, free iodine, or...... 1193

Bromination, of anthranilic acid, 770; of phenyl and tolyl ethers..................1285, 1286

Bromine, hydrolysis of, 937; the basic properties of oxygen compounds with iodine and...... 1330

Bromo-7-acetamino-2-methyl-4-quinazolone.................. 1303

5-Bromoacetoanthranil.................. 772

5-Bromo-2-aminobenzoic acid, 771; barium and silver salts and ethyl ester.................. 772

Bromo-7-amino-2-methyl-4-quinazolone.................. 1303

Bromotantalum compounds.................. 329

Bronzes, analysis of some Bolivian.................. 652

Brown, J. Der elektrische Ofen in Dienste der keramischen Industrie (book).................. 1363, 1537

Browning, P. E. See Gooch, F. A.

Bruce, J. and Harper, H. Practical Chemistry (book).................. 813

Bruner, L and Vorbrodt, J. Einfluss der Lösungsmittel auf die Verteilung der Isomeren (book).................. 813

Bucher. Der Naturwissenschaft (book).................. 895

Bucher, J. E. The acids of the phenylpropiolic series and their condensation to naphthalene derivatives, 212; the constitution of retene and its derivatives.................. 354

Buckminster, I. H. and Smith, E. F. Electrolytic separations.................. 1471

Buchner, G. Die Metallfärbung (book).................. 1363, 1537

Bugge, G. Strahlungserscheinungen, Ionen, Elektronen und Radioaktivät (book).................. 895

Bujwid, O. Mikrophotographischer Wandatlas der Bakteriologie (book).................. 1110

Burette, an adjustable automatic, 703; for standard alkali solutions.................. 971

Burgess, G. K. See Waidner, C. W.

Burgess, L. L. See Richards, T. W.

Burghardt, R. Praktische Anleitung zur Inbetriebsetzung Hoffmannscher Ringofen (book).. 1537

Butanetetracarboxylic acid, ethyl ester of 1058
BUTTERFIELD, W. J. A. See Leeds, F. H.
BUZENAC. Etude sur la corrosion des métaux (book) 1537
BYERS, H. G. The chemical laboratory of the University of Washington (note) 967
BYERS, H. G. and DARRIN, M. The influence of the magnetic field on the passive state of iron .. 750
BYROM, T. H. and CHRISTOPHER, J. E. Modern Coking Practice; Including the Analysis of Materials and Products (book) 727

CADMIUM, rapid determination of, by means of the mercury cathode and stationary anode, 1231; use of organic electrolytes in separation 1251
Cadmium alloys, binary and ternary alloys of bismuth, lead and cadmium 1390
Calcium, revision of the atomic weight of 1577
Calcium bromide, analysis of, 1577, determination of the relation of, to silver bromide 1588
Calcium carbonate, thermal dissociation of 938
Calcium in sea water 647
Calcium phosphates, 869, rate of extraction of plant food constituents from 879
Calcium sulphate, conductance of solutions, 56; solubility of, at high temperatures 50
Calculations, Calculations of General Chemistry (Hale, book), 142; of analysis by means of a calorimetric bomb 552
California section .... Pr. 59, 68, 87, 124
CALMETTE, A. Recherches sur l'épuration biologique et chimique des eaux d'égout (book) ... 1537
Calomel. See Mercury chloride.
Calorimeter, 442, an adiabatic, for use with the calorimetric bomb, 461; for dilution experiments 1179
CAMERON, A. T. Radiochemistry (book), review 1106, title 1110
CAMERON, F. K. and BELL, J. M. The phosphates of calcium (IV) 869
CAMPBELL, J. F. See Sudborough, J. J.
Camphoric acid, derivatives of 1329
Camphor-β-naphthylamidic acid and salts 1322, 1329
Camphoroxalic acid, derivatives of 1499
Camphor series, molecular rearrangements in the 1061, 1064, 1068, 1665, 1669
CANDY, H. C. See Luff, A. P.
Cane sugar. See Sucrose
CANNIZZARO, S. (obituary of) .... Pr. 97
CAPAUN-KARLOWA. Chemisch-technische Spezialitäten und Geheimnisse mit Angabe ihrer Zusammensetzung nach den bewährtesten Chemikern (book) 1110
2-Carbazino-3-amino-4-quinazolone, and hydrochloride and acetyl derivative 127
Carbohydrates, The Simple Carbohydrates and the Glucosides (Armstrong, book) 725
Carbon, atomic weight of, 1, 258, determination of 548
Carbonates, Analyse der Silikat- und Karbonat-Gesteine (Hillebrand, book) 724
Carbon compounds, molecular rearrangements of 1333
Carbon dioxide in sea water 648
Carbon tetrachloride, surface, energy of 1166
m-Carboxyphenylcamphoformenamine 1505, 1515
m-Carboxyphenylcamphoformenaminecarboxylic acid 1504, 1514
CARDARELLI, E. J. See Torrey, H. A.
CARTER, H. A. Ramie China Grass (book) 1008
Catalase of molds 1357
Catalysis, 423; of speed of rearrangements, 1335, on the basis of work with imido esters 221
Cathode, determination of indium with the use of a mercury cathode, 1248; electrolytic determination of chlorine in hydrochloric acid with the use of a silver anode and a mercury cathode, 1468; rapid determinations and separations by means of the mercury cathode and stationary anode, 1628; rapid determination of copper, etc., by means of the mercury cathode and stationary anode, 1231, the mercury cathode, in rapid electroanalysis 637
CAVEN, R. M. Systematic Qualitative Analysis for Students of Inorganic Chemistry (book) .. 248
Ceramic ware, composition of some Greek vases 1259
Cerite, volumetric determination of cerium in 642
Cerium, volumetric determination of, in cerite and monazite 642
CETTOLINI, S. Distillazione del vino ed utilizzazione dei residui della vinificazione (book) ... 1110
CHAMBERS, V. J. See Bogert, M. T.
CHAMOT, E. M. and PRATT, D. S. A study on the phenolsulphonic acid method for the determination of nitrates in water (II) 630

Chapin, W. H. Halide bases of tantalum.. 323
Chaplet, A. See Rousset, H.
Chaplet, A. and Rousset, H. Les succédanés de la soie. Les soies artificielles (book), 248, 1698
Chartier, M. Etude sur la production du caoutchouc dans les colonies Françaises (book)... 1110
Chella, S. See Battelli, A.
Chemical constitution, of retene and its derivatives, 374; relation between, and the optical rotatory power of the sugar lactones, 338; relationship of color and fluorescence to........ 189
Chemical education, section of..Pr. 27
Chemical reagents, a contribution to the history of.................................. 779
Chemical theory, The First Principles of Chemical Theory (Mathewson, book) 143
Chemistry, A Course in Inorganic Chemistry for Colleges (Newell, book), 725; Anleitung zum Experimentieren in der Vorlesung über organische Chemie (Rupe, book), 141; Division of Organic Chemistry, Pr 25, 104, Division of Pharmaceutical Chemistry, Pr. 27, 105; Division of Physical and Inorganic Chemistry, Pr. 23, 103, Einfuhrung in die allgemeine und anorganische Chemie auf elementare Grundläge (Smith, book), 426; Einführung in die Chemie. Ein Lehrbuch für höhere Lehranstalten und zum Selbstunterricht (Ostwald, book), 722; Elementary Modern Chemistry (Ostwald, Morse, book), 574; First Year Chemistry (Segerblom, book), 139; General Chemistry for Colleges (Smith, book), 427, General Inorganic Chemistry (Baskerville, book), 240, History of Chemistry (Thorpe, book), 1693; Introduction to Physical Chemistry (Jones, book), 722; Laboratory Exercises in General Chemistry (Blanchard, book), 1109; Leitfaden für den Unterricht in der anorganischen Chemie didaktisch bearbeitet (Sperber, book), 1534, Neuere Anschaungen auf dem Gebiete der anorganischen Chemie (Werner, book), 1695; Notions fondamentales de chimie organique (Moureu, book), 1362; outline of a theory of organic chemistry founded on the law of entropy, 990, Outlines of Organic Chemistry (Moore, book), 1108; Physical Chemistry for the Electrical Engineers (Morgan, book), 1534, recent advances in organic chemistry (review), 410; Recent Advances in Physical and Inorganic Chemistry (Stewart, book), 574; The Fundamental Principles of Chemistry (Ostwald, book), 572; recent work in biological chemistry, (review) 704
Chesneau, G Theoretical Principles of the Methods of Analytical Chemistry Based upon Chemical Reactions (book) 1110
Chicago section .... Pr 4, 56, 67, 80, 92, 122, 128
Chloral-aniline, condensation of some primary aromatic amines with 973
Chlorides, volumetric method of determining iodide in the presence of bromide, free iodine or.. 1193
Chlorine, atomic weight, 1, 4, 225, 1113; electrolytic determination of, in hydrochloric acid with the use of a silver anode and a mercury cathode, 1468; influence of, upon the determination of nitric nitrogen 756; in sea water... 648
Chlorobenzene, surface energy of....... 1167
p-Chlorophenylcamphoformenamine.. ... .1504, 1513
p-Chlorophenylcamphoformenaminecarboxylic acid. 1503, 1512
Chlorotantalum chloride.... 330
Choline, preparation of, and some of its salts.. 128
Choline acetate.......................... 129
Choline dihydrogen phosphate.. 130
Choline salts, bactericidal properties of lecithins and.................................. 130
Choline sulphate.................... 129
Chowlson, O. D. Traité de physique (book).. 1537
Christiansen, C. and Müller, J. J. Elemente der theoretischen Physik (book).......... 1363
Christopher, J. E. See Byrom, T H.
Chromium, atomic weight of.. ....2, 261
Cillard. See Masselon, R.
Cincinnati section......................................Pr. 7, 47, 60, 68, 82, 88, 129
Cinnamidene-*m*-aminodimethylaniline.. 386
Clark, C. M. Red lines for a balance scale (note) 884
Clark, D. Gold Refining (book)........... 428
Clark, E. D See Sherman, H. C.
Clarke, F. W. A Recalculation of the Atomic Weights (book), 1110; seventeenth annual report of the Committee on Atomic Weights Determinations published during 1909, 255; Stanislao Cannizzaro (obituary)..Pr. 97
Clarke, F. W., Thorpe, T. E., Ostwald, W. and Urbain, G. Report of International Committee on Atomic weights.. 1

Clennell, J. E. The Chemistry of Cyanide Solutions Resulting from the Treatment of Ores (book) ... 813

Cleveland section ... Pr. 8

Clowes, F. and Coleman, J B. Quantitative Chemical Analysis Adapted for Use in the Laboratories of Colleges and Schools (book), review 244, title ... 248

Cobalt, electrolytic determination of, 1632, new volumetric method for ... 757

Coblentz, V. A Manual of Volumetric Analysis (book, review) ... 1693

Codounsky, F. Bierbrauerei (book) ... 1008

Cohn, L. Chemistry in Daily Life (book) ... 248

Coke, action of, on solution of ferric chloride ... 540

Coleman, T. B See Clowes, F.

Coles-Finch, W. Water, its Origin and Use (book) ... 1537

Colligative properties of a solution ... 496

Collis, E. L Lead Smelting (book) ... 1363

Colloidal solutions, Die Methoden zur Herstellung kolloider Losungen anorganischen Stoffe (The Svedberg, book) ... 146

Colloids, Beiträge zu einer Kolloid-chemie des Lebens (Liesegang, book), 1535, Kolloidchemische Beihefte (Ostwald, book), some colloid chemical aspects of digestion, with ultramicroscopic observations ... 680, 245

Color, cause of, in organic compounds, 795; constitution and, 419, relationship of fluorescence and, to constitution ... 189

Color change, relation between the, of indicators and the hydrogen ion concentration ... 822

Colorimetry. See Analysis

Colors, Das Radium und die Farben (Dolter, book) ... 724

Columbus section ... Pr. 91, 128

Composition of some Greek vases ... 1259

Compound, $C_{18}H_{30}O$ ... 88

Condensation of some primary aromatic amines with chloral-aniline, 973; of the acids of the phenylpropiolic series to naphthalene derivatives ... 212

Condensation products of mellitic acid with metaaminophenol ... 189

Conductance, equivalent conductance of ammonium chloride, etc , 161ff; of ammonium acetate solutions at 18, 100 and 156°, 165, at 18, 218 and 306°, 171, of potassium tri-iodide, 914; of saturated solutions of silver chloride, barium sulphate and calcium sulphate ... 53ff.

Conductivity of some concentrated aqueous solutions at zero ... 946

Cone, L H Some recent advances in organic chemistry (review) ... 410

Congress of Applied Chemistry, Eighth International ... Pr 75

Coninck, W O de Cours de chimie minerale (book) ... 1010

Conrad See Pick

Convolvulinolic acid in jalap resin ... 106

Cook A N. Phenyl ether and some of its derivatives ... 1285

Coops, G H. Übersichtliche Darstellung des zweiten Hauptsatzes der Thermodynamik und der daraus herzuleitenden Folgen (book) ... 248

Copper conditions affecting the electrolytic determination of, 1264; rapid determination of, by means of the mercury cathode and stationary anode ... 1231

Copper iodide, the equilibrium between solid cuprous iodide and aqueous solutions containing cupric salt and iodine ... 1207

Copper salts, the equilibrium between solid cuprous iodide and aqueous solutions containing cupric salt and iodine ... 1207

Cordeiro, F J B The Atmosphere, its Characteristics and Dynamics (book) ... 1008

Corliss, H. P. See Parsons, C L.

Cornell section ... Pr 5, 57, 66, 87, 93

Corrections ... 79, 1636

Corson, H P See Parsons, C L

Couturat, L., Lorenz, R and Ostwald, W. International Language and Science (book) ... 1110

Crato, E Massanalyse (book) ... 248

Creuss, W. See Blasdale, W. C

Crinon, C. Revue des médicaments nouveaux et de quelques médications nouvelles (book) ... 1363

Crookes, Sir William. On Scandium (book) ... 1537

Crystallization of hydrazine dioxalate ... 584

Crystallography, Elements of Mineralogy, Crystallography and Blowpipe Analysis (Moses, Parsons, book) ... 144

Cucurbitol ... 90 367

Cuprous nitrate, preparation of a ... 972

Curtiss, R. S. The cause of color in organic compounds ... 795

Curtis, R. W. See Baskerville, C.

CURTMAN, L. J. Some new double arsenates.... 626
CUSHMAN, A. S. and GARDNER, H. A. The Corrosion and Preservation of Iron and Steel (book).... 1110
7-Cyano-2-methyl-4-quinazolone.... 1305
p-Cyano-oxanilic acid, methyl and ethyl esters.... 1498

DAMMER, O. Chemische Technologie der Neuzeit (book).... 1537
DANNEMAN, F. Leitfaden für den Unterricht im chemischen Laboratorium (book).... 248
DARRIN, M. See Byers, H. G.
DAVENPORT, A. L. The estimation of small quantities of nitrogen by Pelouze's reaction.... 1237
DAVIDGE, H. T. Optical Instruments Simply Explained (book).... 1008
DAVIS, A. C. Portland Cement (book).... 248
DAVIS, F. M. New normal solution and reagent bottle (note).... 1277
DELATTRE, S. See Macar, J. de.
DELBRUCK, M. Illustiiertes Brauerei-Lexikon (book).... 1537
DENNERT, E. Das chemische Praktikum (book).... 1363
DENNSTEDT, M. Anleitung zur vereinfachten Elementaranalyse für wissenschaftliche und technische Zwecke (book), 1537; Die Chemie in der Rechtsflege (book).... 1008
Density, of saturated calomel vapor, 1549, of saturated mercury vapor, 1549; of sea water, 648; of silver phosphate, 314; of tantalum chloride.... 1131
DENZ, F. Die Holzverkohlung und der Köhlereibetrieb (book).... 248
DERICK, C. G. Molecular rearrangements of carbon compounds, 1333; see Noyes, W. A.
DESALME, J. and PIERRON, L. Couleurs, peintures et vernis (book).... 895
DESCH, C. H. Metallography (book).... 1008
DESSAU. Die physikalisch-chemischen Eingenschaften der Legierungen (book).... 81
DEVAUD, M. See Rivals, P.
DEWEY, F. P. The solubility of gold in nitric acid.... 318
2,4-Diacetaminobenzohydrazide.... 1309
2,5-Diacetaminobenzoic acid.... 1300
2,4-Diacetamino-*sec.*-butylbenzamide.... 1306
Diacetylhpurganol.... 89
3,4-Diaminobenzonitrile.... 1498
3,6-Diamino-9-hydroxyxanthylbenzene-2-carboxylactone 3,4,5,6-tetracarboxylic acid, and potassium and silver salts.... 197, 198
3,7-Diamino-2-methyl-4-quinazolone.... 1310
sym-Di-(3-amino-4-quinazolone-2-carboxylic acid) hydrazide.... 126
Diastatic power, methods for the determination of.... 1073
Dibenzylamine camphoroxalate.... 1517
3,5-Dibromoacetoanthranil.... 773
3,5-Dibromoacetoanthranilic acid.... 773
3,5-Dibromo-2-aminobenzoic acid, 772; silver salt and ethyl ester.... 773
Dibromo-*m*-tolyl ether.... 1287
Di-*p*-chloroaniline 3,6-dichlorophthalates.... 1320, 1323
3,6-Dichlorophthalanil, preparation of, and of 3,6-dichlorophthalophenylamidic acid.... 1324
3,6-Dichlorophthalic acid, derivatives of.... 1323
3,6-Dichlorophthalophenylamidic acid.... 1324
DICKMANN, K. Der basische Herdofenprozess (book).... 248
Di-*p*-cyano-oxanilide.... 1498
Dietetics, A System of Diet and Dietetics (Sutherland, book).... 145
DIETRICH, H. Untersuchungen über die bei der Elektrolyse von Nickelsalzen auftretenden periodischen Erscheinungen (book).... 1537
Diffusion phenomena of the alums.... 1378
Digestion, some colloid-chemical aspects of, with ultramicroscopic observations.... 680
l-Dihydrohydroxycampholytic acid.... 1669, 1673
DILLING, W. J. Atlas der Krystallformen und der Absorptionsbänder der Hämochromogene (book).... 1698
Dilution, of acid solutions, heat of.... 1176
α,α'-Dimethyladipic acids, synthesis of, and separation of the racemic acid into optical isomers.... 1057, 1060
Dimethylbutanetetracarboxylic acid, ethyl ester of.... 1059
2,5-Dimethylcyclopentanone, preparation of.... 1065
Dimethylphenylethylamine, 761, 766; salts.... 767
Dimethylpyrone, compounds of, and the halogen hydrides.... 542
Dimethyl sulphate, alkylations with.... 761

Dinitro-7-acetamino-2-methyl-4-quinazolone.... 1303
Dinitrohydroquinone, estimation of the intensity of acidity and alkalinity with.... 687
2,4-Dinitro-*p*-phenoxybenzoic acid and silver salt.... 1291
2,4-Dinitrophenyl ether and derivatives 1291
2,4-Dinitrophenylethersulphonic acid and barium salt 1292
Dinsmore, S. C. See Jacobson, C. A.
Dissociation, thermal, of calcium carbonate 938
Dissociation equilibrium. See Equilibrium
Distillation, quantitative, of ammonia by aeration.... 689
Di-*m* toluidine-3,6-dichlorophthalates 1320, 1323
Dodecamethyl - 3,3′,3″,6,6′,6″ - hexamino - 9,9′,9″ - trihydroxy - *sym* - trixanthylbenzene - 2,4,6 - tricarboxylactone, 205, hexahydrochloride of.... 206
Dedecamethyl - 3,3′,3″,6,6′,6″ - hexamino - 9,9′,9″ - trihydroxy - *sym* - trixanthylbenzene - 2,4,6 - tricarboxylic acid, ethyl ester trichloride 207
Dolter, C. Das Radium und die Farben (book), review 724, title 248
Donath, E. Ueber den Ersatz des Schwefelwasserstoffs in der qualitativen chemischen Analyse (book).... 248
Dorset, F. M. Division of Agricultural and Food Chemisty (report) .... Pr. 25
Dover, M. V. See Holmes, M. E.
Dox, A. W. The catalase of molds 1357
Drying, apparatus for drying flasks, etc 650
Duboux, M. Contribution a l'analyse physicochemique des vins (book) 1008
Duclaux, J. La chimie de matière vivante (book).... 1363
Dudley, C. B. (obituary of), Pr., 48, resolutions on death of.... Pr. 32
Duhamel, G. L'acide thyminique (book) 1537
Duhem, P. Thermodynamique et chimie (book) 1110
Duparc, L. and Basadonna, M. Manuel théorique et pratique d'analyse volumétrique (book), review 812, title 727
Durkee, F. W. Experiments in General Inorganic Chemistry (book).... 575
Dyer, B. Fertilizers and Feeding Stuffs (book), 1363, see Spear, E. B.

Easley, C. W. The atomic weight of mercury (II) 1117
Eastern New York section .... Pr. 44, 61, 67, 81, 93, 122, 130
Ehrsam, H. Fabrication des huiles minérales et pyrogénées (book).... 813
Ekeley, J. B. Note on the paper entitled "Some Organic Tungstates" (note).... 541
Electroanalysis: character of silver deposits from various electrolytes, 1571, electrolytic determination of zinc, 530, 533; electrolytic separations, 1471; rapid determinations and separations by means of the mercury cathode and stationary anode, 1628, the mercury cathode in rapid 637
Electrode, effect of different forms of, upon the rate of deposition of copper, 1264, potential of the sodium, 1460, potential of the thallium, ... 732
Electrolytes: character of silver deposits from various, 1571, use of organic, in cadmium separation 1251
Electron conception of valence 1637
Ellis, D. Outline of Bacteriology (Technical and Agricultural) (book), review 726; title 727
Elsden, J. V. Principles of Chemical Geology (book), review 1535; title.... 1537
Elvove, E. Further studies on the application of the Volhard method to the estimation of alkaloids 132
Emery, F. B. Elementary Chemistry (book).... 248
Emmerich, G. H. Lexikon für Photographie u. Reproduktionstechnik (book).... 1008
Ende, C. L. von. See Lewis, G. N.
Ennis, W. D. Linseed Oil and Other Seed Oils (book).... 895
Entropy, outline of a theory of organic chemistry founded on the law of.... 990
Equilibrium between iodine, iodide and polyiodides in aqueous solution, 914; between solid cuprous iodide and aqueous solutions containing cupric salt and iodine, 1207; chemical, 486, 668; does calomel furnish another contradiction of the theory of heterogeneous dissociation equilibrium? 187; heterogeneous equilibria between aqueous and metallic solutions, 502; in the system: potassium iodide, iodine and aqueous alcohol, 1367; the potential of iron calculated from equilibria measurements.... 1214
Erben, F. Vergiftungen, Klinischer Teil, 2 Hälfte: Die organischen Gifte (book) 1537
Erdmann, H. Die Fixierung des Luftstickstoffs und ihre Bedeutung für Ackerbau und Industrie (book), 248; Lehrbuch der anorganischen Chemie (book).... 1363
Escales, R. Chloratsprengstoffe (book), 1698; Die Ammonsalpetersprengstoffe (book).... 428
Escard, J. La fabrication électrochimique de l'acide nitrique et des composés nitrés à l'aide des éléments de l'air (book), 428; Les matières abrasives industrielles (book), 895; Les métaux

spéciaux manganèse, chrome, silicium, tungstène, molybdène, vanadium, et leurs composés métallurgiques industriels (book) 895
Esch, W. See Heil, A.
Esterases, deviation of ferment action from the monomolecular law with special reference to the. 1517
Esters, imido, catalysis on the basis of work with 221
Ether, surface energy of 1165
Ether thioureas and their relation to pseudoammonium bases 1279
Ethoxalylanthranil 122
Ethoxalylanthranilic acid 121
Ethyl acetate, surface energy of 1168
Ethyl alcohol, surface energy of 1170
Ethyl tannate 1312
Euler, H. Allgemeine Chemie der Enzyme (book), 1110; Grundlagen und Ergebnisse der Pflanzenchemie (book) 248
Evans, W. W See Parsons, C. L
Ewell, A. W. A Text-Book of Physical Chemistry: Theory and Practice (book) 428
Ewing, J. A. Die mechanische Kälteerzeugung (book) 1363
Exner, F. Ueber Radiumforschung (book) 1698
Extraction apparatus 1533

Falk, K G. Transference experiments with thallous sulphate and lead nitrate, 1555, see Noyes, A A.
Falk, K G and Nelson, J. M The electron conception of valence 1637
Farrell, F. J. Dyeing and Cleaning (book) 1111
Fats, the determination of the acid value of crude fat and its application in the detection of aged foods 568
Fauvelle La physico-chimie (book) 1537
Fayol, A. Le caoutchouc (book) 428
Feces, preservation of 1683
Fehling's solution 779
Feit, W Ueber die Darstellung des Chlorkaliums aus Hartsalz (book) 575
Felsen, F Der Indigo und seine Konkurrenten (book) 248
Felt, W Ueber die Darstellung des Chlorkaliums aus Hartsalz (book) 248
Fenton, H. J H Outlines of Chemistry with Practical Work (book) 248
Ferchland, P. Die elektrochemischen Patentschriften der Vereinigten Staaten (book) 1008
Ferment action, deviation of, from the monomolecular law with especial reference to the esterases 1517
Fermum. Die Legierungen (book) 428
Fernau, A. Praktische Pharmazie (book) 575
Ferrari, D. Il trattamento naturale ed artificiale delle acque de fonga, secondo i moderni sistemi di epurazione biologica (book) 1009
Ferric ammonium alum, diffusion of 1381
Ferric ammonium arsenate 628
Ferric chloride, action of coke on solutions of 540
Ferric formates 953
Ferrous salts, titration of, in the presence of hydrochloric and phosphoric acids 539
Fertilizer chemistry, division of .... Pr. 25
Fess, F and Steyer, G. A Reconnaissance of the Gypsum Deposits of California (book) 1363
Fichter, F. Uebungen in quantitativer chemischer Analyse (book) 249
Fischer, B. Kurzgefasste Anleitung zu den wichtigeren hygienischen Untersuchungen (book), 1363, Lehrbuch der Chemie für Pharmazeuten (book) 249
Fischer, E Introduction to the Preparation of Organic Compounds (book) 428
Flamand, J. La chimie et la bactériologie du brasseur. Hannut. (book) 727
Flasks, apparatus for drying 650
Fleck, C. Photokeramik (book) 1111
Fleming, L. A. Practical Tanning (book) 1111
Fluorescence, relationship of color and, to constitution 189
Foerster, F. Beiträge zur Kenntniss des elektrochemischen Verhaltens des Eisens (book) 249
Foltzer, J. La soie artificielle et sa fabrication (book) 895
Foods, composition of some Bengali food materials, 558, determination of the acid value of crude fat and its application in the detection of aged foods 568
Foot, F. N. Baking Powder and Other Leavening Agents (book) 575
Foote, H. W. On the formation of double salts 618
Forbes, A. See Henderson, L. J.
p-Formaminobenzonitrile, preparation 1496

7-Formamino-2-methyl 4-quinazolone 1304
Formates, ferric 953
Forrest, L R. See Gill, A H.
Foster, C Le Neve Treatise on Ore and Stone Mining (book) 1009
Foster, W. The composition of some Greek vases 1259
Fowler, A. The Spectrum of Magnesium Hydride (book) 428
Frank, M. Kaufmännisches Handbuch des Photographen (book) 1363
Franke, G. Handbuch der Brikettbereitung (book) 1111
Franke, H. Die pflanzlichen Gerbstoffe Uebersicht über Vorkommen, Eigenschaften, Gewinnung und Anwendung der wichtigeren pflanzlichen Gerbstoffe (book) 895
Frankforter, G. B, Roehrich, V H. and Manuel, E V. The reaction between ammonium chloride and potassium dichromate when heated 178
Franklin, E. C The instability of alloxan (note) 1362
Freezing-point equation 666
Freezing-point lowering, mol numbers derived from 1011
Frémont, C Essais des fers et des aciers par corrosion (book) 1537
Fresenius, H. Chemische Untersuchung der Georgen-, Marien-, Wiesen-, Mariannen- und Friedrichs-Quelle zu Bad Landeck (book) 1009
Frick, J Physikalische Technik oder Anleitung zu Experimental-vorträgen, sowie zur Selbstherstellung einfacher Demonstrationsapparate (book) 727
Friedmann, H. See Goldberg, I
Friedrich, K Mitteilungen aus dem Institut für Metallographie und Probierkunde an der kgl. sächs Bergakademie Freiberg (book) 1698
Friend, J. N. An Introduction to the Chemistry of Paints, with Diagrams (book) 1537
Fries, J A Electric combustion furnace for methane determination 949
Friese, W Tabellen zur Ermittellung der freien Saure, sowie der flüchtigen und nichtfluchtigen Sauren in Wein (book) 575
Fritsch, J Fabrication des engrais chimiques (book), 249, Fabrication du chocolat (book) 895
Frohner, E Lehrbuch der Toxikologie fur Tierarzte (book) 1363
Fructose, protective action of, against the destruction of invertase 988
Fucose, partial stereo-configurations of 345
Fugacity-activity system of Lewis 664
Furnace, electric combustion for methane determination 949

Gadamer, J Lehrbuch der chemischen Toxikologie und Anleitung zur Ausmittelung der Gifte, für Chemiker, Apotheker und Mediziner (book) 249
Gajdeczka, J Lernstoff aus der Physik und Chemie fur Lehramtskandidaten (book) 727
d-Galactose, stereo configuration of 344
Gallotannic acid 1313
Gardner, H A See Cushman, A S.
Garrett, A E The Periodic Law (book) 428
Garrod Thomas, R N See Richards, T.
Garton, F R A High School Course in Physics (book) 1537
Gases, inert, atomic weights 1115
Geisler, E See Moeller, J
Gemmel, G H Chemical Notes and Equations Inorganic and Organic (book) 428
Gentele, J G Lehrbuch der Farbenfabrikation (book) 249
Geography, Neuvième Congrès International de Géographie (book) 811
Geology. Principles of Chemical Geology (Elsden, book) 1535
Georgia section ..... Pr 7, 94, 129
Gerke, O Repetitorium der pharmazeutischen Chemie (book) 249
Gerlach, V Physiologische Wirkungen der Benzoesaure und des benzoesauren Natrons (book) 575
Getman, F H An Introduction to Physical Science (book), review 142, title 575
Gibbs, O W. (obituary of) ..... Pr 69
Gibbs, W. M Spices and How to Know Them (book) 428
Gibbs medal, rules for the award of ..... Pr 120
Giesen, W. Spezialstähle in Theorie und Praxis (book) 249
Gilg, E Lehrbuch der Pharmakognosie (book) 1009
Gill, A. H. and Forrest, L R The hydrocarbons of the wool grease oleins 1071
Gissing, C E. Spark Spectra of the Metals (book) 1537
Gissing, F. T Commercial Peat; Its Uses and Possibilities (book) 428
Glascock, B. L. Metallic strontium 1222
Glazes, analyses of ancient black and red 1259
Glikin, W. Biochemisches Taschenbuch (book) 249
d-Glucose, stereo-configuration of 344

Glucosides, The Simple Carbohydrates and the Glucosides (Armstrong, book).............. 725

GMELIN-KRAUT, New Edition of Gmelin-Kraut's Handbook, Pr., 76; Handbuch der anorganischen Chemie (book)........ 1009

GODFREY, H. Elementary Chemistry (book)........ 249

GOESSMANN, C. A. (obituary of)........ Pr. 131

GOETTLER, H. Praktische Destillateur-Kursus (book)........ 576

Gold, solubility of, in nitric acid........ 318

GOLDBAUM, J S and SMITH, E. F. The electrolytic determination of chlorine in hydrochloric acid with the use of a silver anode and a mercury cathode........ 1468

GOLDBERG, I and FRIEDMANN, H. Die Sulfosäuren des Anthrachinons und seiner Derivate (book)........ 576

GOOCH, F. A. and BROWNING, P. E. Outlines of Qualitative Chemical Analysis (book)...... 428

GORTNER, C V. and R. A. The stereomeric azobenzenes........ 1294

GORTNER, R. A. See Bogert, M. T.

GOTTLIEB, R. See Meyer, H.

GRAFFIGNY, H. DE. La métallurgie électrique (book)........ 249

Grahamite, a solid native bitumen........ 1032

GREAVES, J. E. See Stewart, R.

GREBE. Spektroskopie (book)........ 727

GREDINGER, W. See Stift, A.

GREENLEE, A. D. See Pennington, M. E.

GREER, W. J. Industrial Diseases and Accidents (book)........ 727

GREGORIUS, R. Erdwachs, Paraffin, und Montanwachs, deren Darstellung und Verwendung (book)........ 428

GREINACHER, H. Die neueren Strahlen. Radium-Strahlen, Kathoden-, Kanal-, Anoden-, Röntgenstrahlen. In leichtfasslichen Einzeldarstellungen (book)........ 428

GREINEDER, F. Betreibsbuchfuhrung für Gaswerksbetriebe (book)........ 1363

GRIMMER, W. Chemie und Physiologie der Milch (book)........ 1537

Grindelol........ 90, 368

GROSSMANN, H. and NEUBURGER, A. Die synthetischen Edelsteine (book)........ 1363

GRÜND, G. Organalytische Untersuchungen über den Stickstoff u. Phosphorstoffwechsel in ihre gegenseitigen Beziehungen (book)........ 1698

GRUENER, H. Silver nitrate formed by the action of nitric acid on silver sulphide........ 1030

GRÜNWALD, J. La technique de l'émaillerie moderne (book), 1364; The Theory and Practice of Enamelling on Iron and Steel (book)........ 249

GUARESCHI, R. Fermentazione e fermenti (book)........ 1111

GUERTLER, W. Metallographie (book), review 246, title........ 249

GUEST, H. H. See Johnson, T. B.

GUICHARD, M. Manuel de travaux de chimie minerale (book)........ 1364

GUILLEMINOT, H. Rayons X et radiations diverses (book)........ 1537

GUMBRECHT, O. Wie studiert man Chemie und die beschreibenden Naturwissenschaften? (book)........ 1111

HAENIG, A. Der Graphit (book), 249; Der Schmirgel und seine Industrie (book)........ 249

HAHN, H. Chemie für Techniker. 2 Bd Organische Chemie (book)........ 813

HAIMOVICI, E. Der Eisenbetonbau. 245 Bändchen der Sammlung "Aus Natur und Geisteswelt" (book)........ 576

HALE, W J. Calculations of General Chemistry (book), review 142, title........ 428

Halide bases of tantalum........ 323

Halides of tantalum........ 729

HALL, A. D. Fertilizers and Manures (book)........ 249

HALLOCK, A. P. Report of the Treasurer........ Pr. 19

Halogen halides, compounds of dimethylpyrone and the........ 542

HAMMARSTEN, O. Lehrbuch der physiologischen Chemie (book)........ 813, 1009

HANCKEN, C. W. Dealin, ein neues Antiseptikum (book)........ 1364

HANNEKE, P. Die Herstellung von Diapositiven (book)........ 249

HARKINS, W. D. The Marsh test and excess potential. (I) The quantitative determination of arsenic........ 518

HARPER, H. See Bruce, J.

HARPER, W B. Die Destillation industrielles und forstwirtschaftlicher Holzabfälle (book)... 428

HARRISON, B. H. See Bartow, E.

HART, R. S. Preparation of *o*- and *p*-nitrophenols (note)........ 1105

HARTING, H. Optisches Hilfsbuch für Photographierende (book)........ 249

HARTMANN. See Kirskalt.

HARTMANN, M. L. See Benner, R. C.

Hartwig, C. Die menschlichen Genussmittel, ihre Herkunft, Verbreitung, Geschichte, Bestandteile, Anwendung und Wirkung (book) 1009

Hasterlik, A. Der Tafelsenf (Mostrich) und die technische Verwertung der Senfpflanze (book). 249

Hauberrisser, G. Wie erlangt man brillante Negative und schöne Abdrucke? (book) 727

Hausbrand, E. Hilfsbuch für den Apparatebau (book) 576

Hawk, P. B. See Howe, P. E.; see Rulon, S. A.

Heat, action of, on milk 391

Heat of combustion, of benzene, 280, of sugar, 276; of the octanes and xylenes 268, 289, 293

Heat of dilution of acid solutions 1176

Heat of solution, the adiabatic determination of, of metals in acids, 431, 1176, of metals on concentrated acids, 452; of sodium in mercury, 1466; of zinc 456

Hebing, C. Oelfarbe und Oelfarbenanstriche (book) 249

Hefter, G. Technologie der Fette und Oele (book) 1364

Heidelberger, M. See Metzger, F. J.

Heiduschka, A. and Pfizenmaier, K Beitrage zur Chemie u Analyse der Fette (book) 1537

Heil, A. and Esch, W. Manual pratique de la fabrication du caoutchouc et du produits qui en dérivent (book) 249

Heim, M. Steingutfabrikation (book) 813

Heise, R. See Rost, E. F. F

Hell, G. Pharmazeutisch-technisches Manuale (book) 1111

Henderson, L. J., and Forbes, A. On the estimation of the intensity of acidity and alkalinity with dinitrohydroquinone 687

Henglein, M. Lötrohrprobierkunde (book) 1698

Henle, T. W. Anleitung für das organisch präparative Praktikum (book) review 1245, Anleitung zur organischen Elementaranalyse (book) 727

Hepburn, J. S. See Pennington, M. E.

Herstein, B. Fehling's solution. A contribution to the history of chemical reagents 779

Herz, W. Der Verteilungssatz Mit einer Zusammenstellung der wichtigsten Verteilungskoeffizienten zwischen flüssigen Schichten (book), 576; Sammlung chemischer und chemisch-technischer Vorträge (book) 1698

Herzfeld, J Das Färben und Bleichen von Baumwolle, Wolle, Seide, Leinen, etc (book) 1111

Hesse, O. Ueber die Entwickelung der Industrie der aetherischen Ole in den letzten 25 Jahren. (book) 428

Heuser, E. Ueber Oxalmalonsäureester (book) 727

Hiasiwetz, H Anleitung zur quantitativen chemischen Analyse (book) 249

Higgins, H L. See Benedict, F. G ; see Sherman, H.

Higgins, H. L. and Johnson, A. Elementary analysis by means of a calorimetric bomb 547

Hill, A E. The inconstancy of the solubility product 1186

Hillebrand, W. F. Analyse der Silikat- und Karbonat-Gesteine (book), review 724, title 895

Hillebrand, W. F. and Schaller, W. The Mercury Minerals from Terlingua, Texas (book) .. 1364

Hinrichs, G. D Le Cinquantenaire de l'atomecanique on de la Mécanique des atomes (book review) 812

Hintze, C. Handbuch der Mineralogie (book) 1364

Hönigschmid, O. See Richards, T W

Hoffmann, M. K. Lexikon der anorganischen Verbindungen (book) 895

Holde, D. Untersuchung der Mineralöle und Fette, sowie der ihnen verwandten Stoffe (book) 428

Hollard, A. and Bertlaux, L. Analyse des métaux par electrolyse Métaux industriels; alliages, minerals, produits d'usines (book) 429

Holleman, A F. Die direkte Einführung von Substituenten in den Benzolkern (book), 1111; Lehrbuch der anorganischen Chemie (book), 1698; Lehrbuch der organischen Chemie (book), 1364; Trattato di chimica inorganica (book) 895

Holmes, M. E. and Dover, M. V. The use of organic electrolytes in cadmium separation ... 1251

Homberger, A. W. See Noyes, W. A

Hood, G. F. A First Year's Course of Inorganic Chemistry (book) 1698

Hopkins, C. G. Soil Fertility and Permanent Agriculture (book) 1111

Hort, H. Der Entropiesatz oder der zweite Hauptsatz der mechanischen Wärmetheorie (book) 813

Hough, G. J. Titration of ferrous salts in the presence of hydrochloric and phosphoric acids (note) 539

Howe, J. L. Correction 79

Howe, P. E., Rutherford, T. A. and Hawk, P. B. On the preservation of feces 1683

Hudson, C. S. A relation between the chemical constitution and the optical rotatory power of the sugar lactones, 338; a review of discoveries on the mutarotation of the sugars, 889; Is the hydrolysis of cane sugar by acids a unimolecular reaction when observed with a polariscope? 885; the inversion of cane sugar by invertase. (VI) A theory of the influence of acids and alkalis on the activity of invertase 1220

HUDSON, C. S. and PAINE, H. S. The inversion of cane sugar by invertase. (IV) The influence of acids and alkalies on the activity of invertase, 774; (V) The destruction of invertase by acids, alkalies, and hot water, 985; (VII) The effect of alcohol on invertase............ 1350
HÜBENER, E. Fleischvergiftungen und Paratyphusinfektionen, ihre Entstehung und Verhütung (book).......... 1009
HÜNLICH. Anleitung zur Unterscheidung von Textilmaterialen (book).......... 1537
HUGHES, J. S. and WITHROW, J. R. The character of silver deposits from various electrolytes 1571
HUMPHREY, R. The Fire-Resistive Properties of Various Building Materials (book).......... 1111
Humus acid constituents of soil humus.......... 1674
HUNTER, M. A. Metallic titanium.......... 330
HYDE, B T. B. Division of Industrial Chemists and Chemical Engineers (report).......... Pr. 22
Hydrates, solid, of ammonia.......... 748
Hydration, rate of, of pyrophosphoric acid.......... 1576
Hydrazine, oxalates of.......... 579
Hydrazones, the synthesis of some.......... 1654
Hydriodic acid, reaction between bromic acid and, in presence of much hydrochloric acid, 644; compounds of.......... 546
Hydrobromic acid compounds.......... 545
Hydrocarbons of the wool grease oleins.......... 1071
Hydrochloric acid, reaction between hydriodic acid and bromic acid in the presence of a large amount of, 644; the electrolytic determination of chlorine in, with the use of a silver anode and a mercury cathode, 1468; compounds of.......... 545
Hydrofluoric acid compounds.......... 546
Hydrogen, atomic weight of, 513; determination of.......... 549
Hydrogen ion, relation between the color change of indicators and the concentration of the.......... 822
Hydrogen sulphide, determination of ammonia nitrogen in water in the presence of.......... 1256
Hydrosulphate ion, equivalent conductance of.......... 1141
Hydrolysis, is the hydrolysis of cane sugar by acids a unimolecular reaction when observed with a polariscope? 885, of ammonium acetate at 100 and 156°, 168; ditto at 218 and 306°, 172; ditto at high temperatures, 159; of iodine and of bromine.......... 932
Hydroxylaminoisocampholactone.......... 1667
7-Hydroxy-2-methyl-4-quinazolone.......... 1304
Hydroxypentadecylic acid in jalap resin.......... 106
4-Hydroxyquinazoline-2-carboxylic acid, and ammonium salts and ethyl ester.......... 122, 124
2-*o*-Hydroxystyryl-4-quinazolone.......... 1685

IDDINGS, J. P. Igneous Rocks, Vol I. Their Chemical and Mineral Composition (book) . . 249
Imido esters, catalysis on the basis of work with.......... 221
India rubber chemistry, section of.......... Pr 29
Indiana section.......... Pr. 3, 45, 64, 79, 84, 124, 130
Indicators, chemical nature of, 816; quantitative application of the theory of, to volumetric analysis.......... 815
Indium, determination of indium with the use of a mercury cathode.......... 1248
Industrial Chemists and Chemical Engineers, Division of.......... Pr. 22, 103
Instability of alloxan.......... 809
International Committee, annual report on atomic weights.......... 1113
Inversion of cane sugar by invertase.......... 774, 985, 1220, 1350
Invertase, a theory of the influence of acids and alkalis on the activity of, 1220, destruction of, by acids and alkalies, 778, 985, destruction of, by hot water, 985; effect of alcohol on, 1350; influence of acids and alkalies, 774; inversion of cane sugar by, 774, 985, 1220, 1350; protection of, by fructose.......... 988
Iodide, equilibrium between iodine, iodide, and polyiodides in aqueous solution.......... 914
Iodine, atomic weight of, 2, 257, 1591; compounds of oxygen with, 1330; determination of, in protein combinations, 692, the equilibrium between, iodine, iodide, and polyiodides in aqueous solution, 914, the equilibrium between solid cuprous iodide and aqueous solutions containing cupric salt and, 1207; equilibrium in the system: potassium iodide, aqueous alcohol and, 1367, hydrolysis of, 932; volumetric method of determining iodide in the presence of chloride, bromide or free iodine.......... 1193
Ion, the ionization of salts in mixtures with no common ion.......... 741
Ionic theory, the properties of salt solutions in relation to the.......... 1011
Ionization, correlation of rearrangements with free energy of, 1335; of ammonium hydroxide and acetic acid, 164; of potassium tri-iodide, 914; of salts in mixtures with no common ion,

741; of water at 100 and 156°, 168; of water at 218 and 306°, 172; of water at high temperatures 159
Ionization constants, values of the, of indicators 858
Ionization relations of sulphuric acid 1133
Iowa section .... Pr. 45, 86
Ipurganol, a new dihydric alcohol 89, 368
Ipurolic acid, in jalap resin 107
Iridium, atomic weight of 266
Iron, colorimetric determination of manganese in presence of, 965; electrolytic determination of, 1634; influence of the magnetic field on the passive state of, 750, potential of calculated, from equilibria measurements, 1214; retention of arsenic by 519, 522
Iron group, precipitation of 953
Isham, R. M. See Barneby, O. L.
Isocampholactone 1665
β-Isocamphoramidic acid 1671
Isocamphoric acid, derivatives of, 1669, 1670, 1671; preparation of 1670
l-Isocamphoric acid, α-monomethyl ester, 1670; dimethyl ester, 1671; methyl ester amide 1671
Isodihydroaminocampholytic acid and hydrochloride and lead salt 1672

Jabs, A. Torfkoks und Kraftgas (book) 250
Jacobson, C. A. and Dinsmore, S. C. An improved siphon (note) 810
Jaeger, H Die Bakteriologie des täglichen Lebens (book) 429
Jänecke, E Gesättigte Salzlösungen vom Standpunkt der Phasenlehre (book), 250; Kurze Uebersicht über sämtliche Legierungen (book), 1009; Summary of Alloys The Employment of Physical Chemistry in Metallography (book) 429
Jago, W. A Manual of Forensic Chemistry, Dealing Especially with Chemical Evidence, Its Preparation and Adduction (book) 429
Jahr, H. Anleitung zum Entwerfen und zur Berechnung der Standfestigkeit von Fabrikschornsteinen aus Mauerwerk, Eisen und Eisenbeton, nebst den hierüber erlassen Bestimmungen und die rauchfreie Verbrennung bei Dampfkesseln (book) 576
Jaksch, R v Die Vergiftungen (book) 1537
Jalap, chemical examination of 80
James, C. Thulium 517
James, C and Pratt, L A Basic nitrate of yttrium 873
Jamieson, G. S. On a new volumetric method for cobalt and nickel 757
Javillier, M Les ferments protéolytiques Etude chimique et pharmacotechnique (book) 813
Jenke, F. Die volkswirtschaftliche Bedeutung des künstlichen Indigos (book) 576
Jenks, T. Chemistry for Young People (book) 429
Jesse, R. H., Jr. See Richards, T. W.
Jodidi, S. L. Organic nitrogenous compounds in peat soils 396
Jörgensen, A. Die Mikroörganismen der Gärungsindustrie (book) 250
Johnson, A See Higgins, H L.
Johnson, J. P. Ore Deposits of South Africa (book) 1111
Johnson, T. B and Guest, H H. Metathetical reactions: ether thioureas and their relation to pseudoammonium bases, 1279, researches on amines, alkylations with dimethyl sulphate. Synthesis of dimethylphenylethylamine 761
Johnston, J. The thermal dissociation of calcium carbonate, 938; see Allen, E. T
Joly, A. Manipulations chimiques (book) 1009
Jones, G. The atomic weight of hydrogen, 513; see Baxter, G. P.
Jones, H. C. Introduction to Physical Chemistry (book), review 722, title 895
Jones, L. and School, F. J. The Manufacture of Cane Sugar (book) 429
Jordan, S. The condensation of some primary aromatic amines with chloral-aniline 973
Jurisch, K. W. Ueber Luftsalpeter (book) 813

Kahane, M. Die Arzneitherapie der Gegenwart (book) 1538
Kahlenberg, L. Laboratory Exercises in General Chemistry (book), 727; Outlines of Chemistry: a Text-book for College Students (book) 250
Kahnert, P. Durchführung des Roheisen-Erz-Prozesses im Martinofen (book) 1364
Kansas City section .... Pr. 6, 57, 66, 86, 92, 129
Karsten, J. and Oltamus, F Lehrbuch der Pharmakognosie (book) 250
Kassel, R. Viskosität binarer Flussigkeitsgemische (book) 1538
Kato, Y. See Noyes, A. A.
Kauffmann, H. Das Radium u. die Erscheinungen der Radioaktivität (book) 1364
Kautny, T. Handb. der autogenen Schweissung (book) 1364
Kayser, H. Handbuch der Spektroskopie (book) 1699

Keane, C. A. Modern Organic Chemistry (book) 429
Kedesdy, E. Die Sprengstoffe. Darstellg. u. Untersuchg. der Sprengstoffe u. Schiesspulver (book) 250
Keiser, E. H. and McMaster, LeRoy. The action of magnesium upon the vapors of organic compounds 388
Kellas, A. M. Introduction to Practical Chemistry for Medical, Dental and General Students (book) 250
Kendall, E. C. See Sherman, H. C.
Kendall, E. C. and Sherman, H. C. Studies on amylases. (II.) A study of the action of pancreatic amylase 1087
Kielmeyer, A. Der Farberlehrling im Chemie-Examen (book) 1364
Kienitz-Gerloff, F. Botanisch-mikroskopisches Praktikum (book) 1364
Kietaibl, K. Das Generatorgas; seine Erzeugung und Verwendung (book) 1111
Kimley, W. S. The mercury cathode in rapid electroanalysis 637
King, A. S An Electric Furnace for Spectroscopic Investigations, with Results for the Spectra of Titanium and Vanadium (book) 250
Kipping, F. S. and Perkin, W. H. Inorganic Chemistry (book) 250
Kirchner, O. Die kaustische und kohlensaure Verseifung in der modernen Seifenindustrie. Die Haushaltungsseife (book) 813
Kirk, E. The Cupola Furnace (book) 1699
Kirskalt, and Hartmann. Praktikum der Bakteriologie und Protozoologie (book) 250
Klar, M. Technologie der Holzverkohlung (book) 727
Klein, J H. Ueber Vorkommen und Herkunft des Inosit im Tierkörper (book) 727
Knecht, E. A Manual of Dyeing (book) 727
Knight, L. See Noyes, W. A.
Knorr, E. Leitfaden der Chemie für Brauer und Mälzer (book) 250
Kober, P. A. The quantitative distillation of ammonia by aeration. (II) 689
Koch, J. Dispersionsmessungen an Gasen im sichtbaren und im ultraroten Spektrum (book) .. 429
König, J. Chemie der menschlichen Nahrungs- und Genussmittel (book) 727
Kohl, F. G. Ueber das Wesen der Alkoholgärung (book) 1538
Kollock, L. G. and Smith, E. F. The determination of indium with the use of a mercury cathode 1248
Kraft, E. Analytisches Diagnostikum. Die chemischen, mikroskopischen und bakteriologischen Untersuchungsmethoden von Harn, Auswurf, Magensaft, Blut, Kot (book) 250
Kraus, A. and Schwenzer, P. Hilfstabelle für Nahrungsmittelchemiker (book) 1538
Kraus, C. A. See Lewis, G. N.
Kremann, R. Leitfaden der graphischen Chemie. Erläuterung einiger wichtiger Schulbeispiele (book) 1699
Krönlein, H. Lederfabrikation (book) 813
Krüss, G. und H. Kolorimetrie und quantitative Spektralanalyse in ihrer Anwendung in der Chemie (book) 250
Küspert, F. Lehrgang der Chemie und Mineralogie für höhere Schulen (book) 727
Kurz, K. Der Radiumvorrat der Natur (book) 1538
Kyriakides, L. P. See Noyes, W. A.

Laboratory, chemical, of the University of Washington 967
Lachaud, M. Nouvelle théorie des sciences physiques. Unité de la matière, étude des fluides (book) 1538
Lactones, relation between the chemical constitution and the optical rotatory power of the sugar lactones 338
Lactonic ring, proof of the position of 345
Lamb, A. B. The potential of iron calculated from equilibria measurements 1214
Landolt, H. Ueber die Erhaltung der Masse bei chemischen Umsetzungen (book) 250
Landsberger, F. Ueber Nitrocumarine und ihre Konstitutionsermittelung (book) 1364
Lange, H. Studien über die Zusammensetzung heliumführender Mineralien (book) 1538
Lathrop, E. C. See Shorey, E. C.
Latta, M. N. American Producer Gas Practice and Industrial Gas Engineering (book) 813
Laubenheimer, K. Phenol und seine Derivate als Desinfektionsmittel (book) 250
Lauber, E. Praktisches Handbuch des Zeugdrucks (book) 1111
Laurolene, mechanism of the reactions by which it is formed, 1068; oxidation products of *d*- and *l*-, 1061; structure of, 1064; synthesis of, 1064; synthetic 1066
Lavaux, J. Sur une association naturelle de diméthylanthracènes (book) 813
Law, deviation of ferment action from the monomolecular law with especial reference to the

esterases, 1517; fundamental law for a general theory of solutions, 653, 1636; outline of a theory of organic chemistry founded on the law of entropy.... 990
Leach, A. E. Food Inspection and Analysis (book).... 576
Lead alloys, binary and ternary alloys of cadmium, bismuth and lead.... 1390
Lead nitrate, transference data for, 1565; transference experiments with thallous sulphate and.. 1555
Lean, B. See Perkin, W. H.
Le Blanc, M. Die elektromotorischen Kräfte der Polarisation und ihre Messung mit Hilfe des Aszillographen (book).... 727
Lecithins, bactericidal properties of choline salts and.... 130
Leeds, F. H. and Butterfield, W. J. A. Acetylene: The Principles of Its Generation and Use (book).... 727
Lehigh Valley section....Pr. 8
Lehmann, F. Ueber massanalytische Methoden zur Bestimmung der Zuckerarten (book).. .. 1538
Lehmann, K. Die Fabrikation des Surrogatkaffees und des Tafelsenfes (book).... 1364
Lehmann, L. See Witt, O. N.
Lehmann, O. Flüssige Krystalle, Myelinformen und Muskelkraft (book).... 814
Lehner, S. Die Kitte und Klebemittel (book).... 250
Leimbach, R. Die ätherischen Oele. Monographien über chemisch-technische Fabrikationsmethoden (book).... 1364
Leiser, R. Elektrische Doppelbrechung der Kohlenstoffverbindungen (book).... 1538
Lenard, P. Ueber Aether und Materie (book).... 1699
Lenhartz, C. Mikroskopie und Chemie am Krankenbett (book).... 1538
Levene, P. A. On the biochemistry of nucleic acids.... 231
Lewis, E. J. Qualitative Analysis Tables for Use at the Bench (book).... 1111
Lewis, G. N. The theory of the determination of transference numbers by the method of moving boundaries.... 862
Lewis, G. N. and Ende, C. L. von The potential of the thallium electrode.... .. 732
Lewis, G. N and Kraus, C. A. The potential of the sodium electrode.... 1459
Lewis, J See Wedekind, E.
Leyser, E. Die Malz- und Bierbereitung (book).... 1009
Liebetanz, F. Calciumcarbid-Fabrikation (book).... 250
Liesegang, von R. E. Beiträge zu einer Kolloidchemie des Lebens (book), review 1535, title. 429
Liess, O. Beitrag zur Kenntniss der Wirkung der Formaethrolpraparate (book).... 1364
Life, Beiträge zu einer Kolloidchemie des Lebens (Liesegang, book).... 1535
Light, some chemistry of.. 147
Lignoceric acid, $C_{24}H_{48}O_2$.... 1679
Lindner, P. Atlas der mikroskopischen Grundlagen der Gärungskunde (book).... 1538
Linschmann, H. Die Spiritusindustrie, ihre Technik, Steuern and Monopole (book).... ... 250
Lipski, J Ueber Synthese des Ammoniaks aus den Elementen (book).... 1699
Liquids, determining under constant condition the boiling points of minute quantities of, 897; determining vapor pressures and boiling points of, at standard pressures, 907, static method for determining the vapor pressures of.... 1412
Lithium, atomic weight of, 4, 1114; history of the revisions of the atomic weight of.... .. 10
Lithium chloride, conversion of, into perchlorate, 37; drying and weighing of, 25; ratio of oxygen to, 35; ratio of, to silver, 31; ratio of, to silver chloride and silver.... 4
Lithium perchlorate, conversion of lithium chloride into.... 37
Lockemann, G. Die Beziehungen der Chemie zur Biologie und Medizin (book).... 250
Lodin. Note sur la fabrication électrolytique de l'aluminium (book).... 1538
Loeb, M. Oliver Wolcott Gibbs (obituary)....Pr. 69
Loeb, M. and Morey, S. R. Analysis of some Bolivian bronzes.... 652
Löb, W. Einführung in die chemische Wissenschaft (book).... 250
Löhnis, F. Handbuch der landwirtschaftlichen Bakteriologie (book) review 1108
Löscher, F. Vergrössern und Kopieren auf Bromsilberpapier (book).... 250
Löwenstein, E. Ueber Hydrate, deren Dampfspannung sich kontinuierlich mit der Zusammensetzung ändert (book) 1538
Loock. Chemie und Photographie bei Kriminalforschungen (book).... 727
Lord, J. P. Radium (book).... 1538
Lorenz, H. Lehrbuch der technischen Physik (book).... 1009
Lorenz, R. See Couturat, L.
Louisiana section....Pr. 4, 46, 58, 65, 82, 92, 124, 127
Louisville section....Pr. 7, 59, 80, 91
Love, E. G. Report of the Librarian for the year 1909....Pr. 22
Low, A. H. Technical Methods of Ore Analysis (book).... 429
Luff, A. P. and Candy, H. C. A Manual of Chemistry, Theoretical and Practical, Inorganic and Organic (book).... 1364

Lukaszczyk, J. Beiträge zur Erzaufbereitung (book).................... 1364

Lunge, G. Coal Tar and Ammonia (book), 576; The Manufacture of Sulphuric Acid and Alkali, with the Collateral Branches (book).................... 576

Lunge, G. and Beri, E. Chemisch-technische Untersuchungsmethoden (book).................... 728

Lusk, G. The Elements of the Science of Nutrition (book), review 1007; the fate of the amino acids in the organism.................... 671

McAdam, D. J., Jr. The atomic weight of vanadium.................... 1603

Macar, J. de and Delattre, S Les explosifs militaires violents (book).................... 1364

McCay, L. W. The analysis of tin-antimony alloys.................... 1241

McClung, R. K. Conduction of Electricity through Gases, and Radioactivity; a Text-book with Experiments (book).................... 728

McCrackan, R. F. See Metzger, F. J.

McDermott, F. A. The preparation of platinum black.................... 336

MacEwen, H. A. Food Inspection. A Practical Handbook (book).................... 728

Macfarlane, W. Laboratory Notes on Iron and Steel Analysis (book).................... 250

McGregory, J. F. A Manual of Qualitative Analysis (book), review 243, title.................... 429

Mach, E. Populärwissenschaftliche Vorlesungen (book).................... 1538

McIntosh, D. The basic properties of oxygen· compounds of dimethylpyrone and the halogen hydrides, 542; compounds with bromine and iodine.................... 1330

McIntosh, J. G. Indiarubber and Gutta-Percha (book).................... 1009

MacKay, G M. J. See Bray, W. C.

McKee, R. H Division of Organic Chemistry (report)....................Pr. 25

MacKnight, E F. Fertilizer and Acid Plants (book).................... 429

McMaster, Le Roy. See Keiser, E. H.

McMillan, W. G A Treatise on Electrometallurgy (book).................... 1538

MacRae, D. See Mills, J E.

Mäkelt, E. Die Stromerzeugung durch fallende Teilchen in Flüssigkeiten und der absolute Nullpunkt des Potentials (book).................... 1111

Magnesium, action of, upon the vapors of organic compounds, 388; in sea water.................... 647

Magnetic field, influence of, on the passive state of iron.................... 750

Manganese, new volumetric method for the determination of, 1250; colorimetric determination of, in presence of iron.................... 965

Mann, H. Die moderne Parfümerie (book).................... 728

Mannheim, E. Toxikologische Chemie (book).................... 814

Manning, R. J. Ethyl tannate.................... 1312

d-Mannose, stereo-configuration of.................... 344

Manuel, E. V. See Frankforter, G. B.

Marr, O. Das Trocken u. die Trockner (book).................... 1009

Marsh test.................... 518

Masing, G. Ueber die Bildung von Legierungen durch Druck und über die Reactionsfähigkeit der Metalle im festen Zustande (book).................... 1538

Mason, W. P. Examination of Water (Chemical and Bacteriological), (book).................... 1364

Masselon, R. and Cillard. Le celluloid, fabrication, applications, substituts (book).................... 1699

Mathers, F. C. The preparation of perchloric acid from sodium perchlorate.................... 66

Mathewson, C. H. The First Principles of Chemical Theory (book), review.................... 143

Mauraln, C. Les états physiques de la matière (book).................... 1538

Meat, an application of the Folin method to the determination of the ammoniacal nitrogen in.. 561

Medal, rules for award of the Willard Gibbs medal....................Pr. 120

Medicus, L. Einleitung in die chemische Analyse (book).................... 1538

Mees, C. E. K. An Atlas of Absorption Spectra (book).................... 251

Meigen, W. Uebungsbeispiele zur quantitativen Analyse (book).................... 728

Melcher, A. C. The solubility of silver chloride, barium sulphate, and calcium sulphate at high temperatures.................... 50

Mellitic acid, condensation products of, with *m*-aminophenol.................... 189

Mellmann, P. Chemie des täglichen und wirtschaftlichen Lebens (book).................... 1009

Members deceased....................Pr. 8, 47, 61, 69, 82, 94, 97, 113, 131

Members elected....................Pr. 1, 40, 51, 63, 77, 83, 89, 95, 110, 113, 121, 125

Mendeléef, D. Versuch einer chemischen Auffassung des Weltäthers (book).................... 1538

Mengarini, Traube, M. and Scala, A. Ueber die chemische Durchlässigkeit lebender Algen- und Protozoenzellen für anorganische Salze und die spezifische Wirkung letzterer (book)... 429

Menzies, A. W. C. A convenient form of apparatus for the measurement of the vapor densities of easily volatil substances, 1624; a method for determining the molecular weights of dissolved substances by measurement of lowering of vapor pressure, 1615; see Smith, A.

Mercury, action of thionyl and sulphuryl chlorides on, 184; atomic weight of, 2, 263, 1117; boiling point of, 1446; density of saturated vapor, 1549; heat of solution of sodium in, 1466; purification of, 971; redetermination of the vapor pressures of, from 250–435°, 1434, 1439; solubility of calomel vapor in 1554

Mercury cathode. See Cathode.

Mercury chloride, density of saturated calomel vapor, 1549; does calomel furnish another contradiction of the theory of heterogeneous dissociation equilibrium? 187; quantitative study of the constitution of calomel vapor, 1541; vapor pressures of calomel 1546

Mercury oxide, action of thionyl and sulphuryl chlorides on mercuric oxide 184

Metallography, Metallographie: Ein Ausführliches Lehr- und Handbuch der Konstitution und der physikalischen, chemischen und technischen Eigenschaften der Metalle und metallischen Legierungen (Guertler, book), 246; The Elements of Metallography (Ruer, book) 246

Metals, adiabatic determination of heats of solution of, in acids, 431, 1176, heat of solution of, in concentrated acids, 452; retention of arsenic by 519

Methane, electric combustion furnace for determination of 949

Methoxalylanthranil 121

Methoxalylanthranilic acid 120

Methoxycamphoroxalic acid, methyl ester 1508

2-*m*-Methoxy-*p*-hydroxystyryl-4-quinazolone 1658

Methyl alcohol, surface energy of 1170

2-Methyl-3-benzalamino-4-quinazolone and hydrochloride 1659

2-Methyl-3-cinnamalamino-4-quinazolone 1660

4-Methyl-2′,4′-dinitrophenyl ether, and its sulphonic acid derivative, 1289, salts of the latter 1290

Methyl formate, surface energy of 1168

Methyl-*p*-nitrophenylethylamine 768

3-Methyl-4-quinazolone-2-carbomethylamide 124

2-Methyl-3-salicalamino-4-quinazolone, and potassium salt and hydrochloride 1661

Methylsulphuric acid, phenylethylammonium salt of 766

2-Methyl-3 vanillalamino-4-quinazolone 1661

Metzger, F. J. and Heidelberger, M. The volumetric determination of cerium in cerite and monazite 642

Metzger, F. G and McCrackan, R. F A new volumetric method for the determination of manganese 1250

Meusel, E. Die Materie der chemischen Elemente und das Wesen der chemischen Reaction (book) 1538

Meyer, D Die Kalk und Magnesiadüngung (book) 1111

Meyer, F. Die Technik der Verbrennung und Energiegewinnung aus städtischen Abfallstoffen (book) 1538

Meyer, G Chemie und landwirtschaftl. Nebengenwerbe (book) 1365

Meyer, H. und Gottlieb, R Die experimentelle Pharmakologie als Grundlage der Arzneibehandlung (book) 1009

Meyer, J. Die Allotropie der chemischen Elemente (book) 1009

Meyer, W Ausgewählte Kapitel über Chemie (book) 251

Michael, A Outline of a theory of organic chemistry founded on the law of entropy 990

Michaelis, L. Dynamik der Oberflächen. Eine Einführung in biologische Oberflächenstudien (book) 251

Michaelissen Der Erhärtungsprozess der kalkhaltigen hydraulischen Bindemittel (book) 251

Michel, F. Ueber die Reaktion zwischen Sulfurylchlorid und Ammoniak (book) 1699

Michigan section .... Pr. 130

Mie, G. Lehrbuch der Elektrizität und des Magnetismus (book) 1365

Milk, action of heat on 391

Miller, J. B. Glasätzerei (book) 251

Mills, J. E. and MacRae, D. On surface energy and surface tension 1162

Milwaukee section .... Pr. 7, 59, 81, 86, 112

Mindes, J. Selbsbereitung pharmazeutischer Spezialitäten (book) 429

Mineralogy, Elements of Mineralogy, Crystallography and Blowpipe Analysis (Moses, Parsons, book) 144

Mineral oil. See Petroleum.

Minkowski, E. Ueber das Verhalten einiger aromatischer Essigsäure- und Glykollderivate tierischen Fermenten gegenüber (book) 251

Minnesota section .... Pr. 8, 61, 68, 82, 111, 127

Minz, S. G. Zur Frage von dem Einfluss der Milchnahrung auf den Stickstoff- und Phosphorumsatz (book) 1538

Missouri section .... Pr. 3, 59, 84, 91

Mitchell, C. A. Oil: Animal, Vegetable, Essential and Mineral (book) 1365, 1538

Mitreiter, M. Die Gewinnung des Broms in der Kaliindustrie (book) 814

Mittelstaedt, O. Technical Calculations for Sugar Works (book)........ 1111
Moeller, J. und Geisler, E. Real-Enzyklopädie der gesamten Pharmazie (book)........ 1111
Mohr, E. Anleitung zum zweckmässigen Rechnen bei chemischen präparativen Arbeiten (book). 251
Molds, the catalase of........ 1357
Molecular rearrangements in the camphor series........ 1061, 1064, 1068, 1665, 1669
Molecular weight, method for determining the, of dissolved substances by measurement of lowering of vapor pressure, 1615; of calomel in solution in mercury........ 1554
Molisch, H. Die Eisenbakterien (book)........ 1538
Moll, R. Beitrage zur Biochemie des Bodens (book)........ 814
Mol numbers derived from the freezing-point lowering........ 1011, 1026, 1027, 1029
Monazite, volumetric determination of cerium in........ 642
Moor, C. G. The Recognition of Minerals (book)........ 251
Moor, C. G and Partridge, W. Aids to the Analysis of Food and Drugs (book)........ 251
Moore, C. J. The purification of mercury (note)........ 971
Moore, F. J. Outline of Organic Chemistry (book), review 1108; title 1365; the colored salts of Schiff bases (III)........ 382
Moore, R. B. See Schlundt, H.
Moraucé, E. Composition chimique des alcools d'industrie et des spiritueux (book)........ 251
Morden, G. W. Die Stickoxybildung aus Luft mit Hilfe einer Gleichstromentladung niedriger Spannung unter vermindertem Druck (book)........ 728
Morey, S. R. See Loeb, M.
Morgan, J. J. Blast Furnace Practice (book)........ 429
Morgan, J. L. R. Physical Chemistry for the Electrical Engineers (book), review........ 1534
Morse, H. W. See Ostwald, W.
Moser, A. Die elektrolytischen Prozesse der organischen Chemie (book)........ 1365
Moser, L. Die Bestimmungsmethoden des Wismuts und seine Trennung von den anderen Elementen (book)........ 429
Moses, A. J. and Parsons, C. L. Elements of Mineralogy, Crystallography, and Blowpipe Analysis (book), review........ 144
Moureu, C. Notions fondamentales de chimie organique (book), review 1362, title........ 1699
Moving boundaries, theory of the determination of transference numbers by the method of.... 862
Muccioli, A. Tossicologia forense (book)........ 1009
Müller, J. J. See Christiansen, C.
Mulliken, S. P. A Method for the Identification of Pure Organic Compounds. Vol. 3. Identification of the Commercial Dyestuffs (book), 1365; progress in systematic qualitative organic analysis........ 1049
Murray, B. L. Division of Pharmaceutical Chemistry (report)........ Pr. 27
Murray, J. A. Soils and Manures (book)........ 1365
Mutarotation, a review of discoveries on the, of the sugars........ 889
Myer, O. Handbuch der Kaliwerke, Salinen, Tiefbohrunternehmungen und Petroleum Industrie (book)........ 895

Nagel, O. The Transportation of Gases, Liquids and Solids, by Means of Steam, Compressed Air and Pressure Water (book)........ 429
Naphthalene derivatives, condensation of the acids of the phenylpropiolic series to........ 212
1(Naphthol-1)-1-keto-3-hydroxy-3(6-nitro-3,4-methylendihydroxyphenyl)-propane, and derivatives........ 1485, 1487
β-Naphthoquinone, note on the oxidation of........ 117
Naphthotetrazines (review)........ 793
β-Naphthylimide........ 1320
3-β-Naphthyl-4-β-naphthyliminoquinazoline-2-carboxylic acid, ethyl ester........ 126
Nebraska section........ Pr. 5, 80, 93, 129
Nelson, B. E. Introduction to the Analysis of Drugs and Medicines (book)........ 1365
Nelson, J. M. See Falk, K. G.
Nernst lamp........ 155
Neuburger, A. See Grossmann, H.
Neumann, A. Analyse und Antidote der für den Arzt wichtigsten Gifte (book)........ 1111
New Books: Reviews—First Year Chemistry (Segerblom), 139; Anleitung zum Experimentieren in der Vorlesung über organische Chemie (Rupe), 141; Calculations of General Chemistry (Hale), 142; An Introduction to Physical Science (Getman), 142; The First Principles of Chemical Theory (Mathewson), 143; Elements of Mineralogy, Crystallography and Blowpipe Analysis (Moses, Parsons), 144; Annuaire pour l'An 1910, 144; A System of Diet and Dietetics (Sutherland), 145; Die Methoden zur Herstellung kolloider Lösungen anorganischen Stoffe (Svedberg), 146; General Inorganic Chemistry (Baskerville), 240; Experimentelle Untersuchungen über Atomgewichte (Richards), 242; Treatise on Qualitative

Analysis (Sellers), 242; A Manual of Qualitative Analysis (McGregory), 243; An Introduction to Chemical Analysis for Students of Medicine, Pharmacy and Dentistry (Rockwood), 243; Quantitative Chemical Analysis: Adapted for Use in the Laboratories of Colleges and Schools (Clowes, Coleman), 244; Anleitung für das organisch präparative Praktikum (Henle), 245; Kolloid-chemische Beihefte (Oswald), 245; Metallographie: Ein ausführliches Lehr- und Handbuch der Konstitution und der physikalischen, chemischen und technischen Eigenschaften der Metalle und metallischen Legierungen (Guertler), 246; The Elements of Metallography (Ruer), 246, Einführung in die allgemeine und anorganische Chemie auf elementare Grundläge (Smith), 426; General Chemistry for Colleges (Smith), 427; The Fundamental Principles of Chemistry (Ostwald), 572; Elementary Modern Chemistry (Ostwald, Morse), 574; Recent Advances in Physical and Inorganic Chemistry (Stewart), 574; Introduction to Physical Chemistry (Jones), 722; Einführung in die Chemie. Ein Lehrbuch für höhere Lehranstalten und zum Selbstunterricht (Ostwald), 722; Analyse der Silikat- und Karbonat-Gesteine (Hillebrand), 724; Das Radium und die Farben (Dölter), 724; The Simple Carbohydrates and the Glucosides (Armstrong), 725, A Course in Inorganic Chemistry for Colleges (Newell), 725; Outline of Bacteriology (Technical and Agricultural) (Ellis), 726; Neuvième Congrès International de Géographie, 811; Wall Charts for Sugar Chemists (Rodger), 811, Le Cinquantenaire de l'atomecanique ou de la mècanique des atomes (Hinrichs), 812; Manuel théorique et pratique d'analyse volumétrique (Duparc, Basadonna), 812; The Elements of the Science of Nutrition (Lusk), 1007, Radiochemistry (Cameron), 1106; Outlines of Organic Chemistry (Moore), 1108; Handbuch der landwirtschaftlichen Bakteriologie (Löhnis), 1108; Laboratory Exercises in General Chemistry (Blanchard), 1109, Notions fondamentales de chimie organique (Moureu), 1362; Physical Chemistry for the Electrical Engineers (Morgan), 1534; Leitfaden für den Unterricht in der anorganischen Chemie didaktisch bearbeitet (Sperber), 1534; Beiträge zu einer Kolloidchemie des Lebens (Liesegang), 1535, Principles of Chemical Geology (Elsden), 1535, A Manual of Volumetric Analysis (Coblentz), 1693; History of Chemistry (Thorpe), 1693; Neuere Anschauungen auf dem Gebiete der anorganischen Chemie (Werner), 1695; Die Alkaloide Eine Monographie der natuerlichen Basen (Winterstein, Trier).............. 1696

NEW BOOKS TITLES—*Biographical and Historical*: The Story of Sugar (Surface), 253, The Story of Oil (Tower), 253; A History of Chemistry (Armitage), 428, History of Chemistry (Thorpe), 430; L'évolution de la chimie (Ostwald), 895; Ursprung und Entwicklung der chemischen Industrie (Binz), 1008; Le Centenaire du Journal de Pharmacie et de Chimie (Bourquelot), 1008; Lavoisier und seine Vorläufer (Speter), 1112, The Life of William Thompson, Baron Kelvin of Largs (Thompson), 1112, Zur Geschichte des Tellures (Bauer), 1363; Aus pharmazeutischer Vorzeit (Peters) 1365

General and Inorganic: Elementary Chemistry (Godfrey), 249; Beiträge zur Kenntniss des elektrochemischen Verhaltens des Eisens (Foerster), 249; Outlines of Chemistry with Practical Work (Fenton), 248; Elementary Chemistry (Emery), 248; Das Radium und die Farben. Einwirkung des Radiums und ultravioletter Strahlen auf organische und anorganische Farben sowie auf Mineralien (Doelter), 248; Leitfaden für den Unterricht im chemischen Laboratorium (Danneman), 248; Uebersichtliche Darstellung des zweiten Hauptsatzes der Thermodynamik und der daraus herzuleitenden Folgen (Coops), 248; Chemistry in Daily Life (Cohn), 248; Stöichiometrie (Bornemann), 248, Die Untersuchungsmethoden des Wasserstoffperoxyds (Birckenbach), 248; Chemisches Praktikum für Anfänger (Binz), 247; Ueber einige Adsorptionserscheinungen (Behre), 247; First Stage Inorganic Chemistry (Bausor), 247; First Stage Inorganic Chemistry (Bailey), 247; Theorien der Chemie (Arrhenius), 247; Handbuch der anorganischen Chemie, in 4 Bänden (Abegg, Auerbach), 247; Gesättigte Salzlösungen vom Standpunkt der Phasenlehre (Jänecke), 250; Outlines of Chemistry; a Text-book for College Students (Kahlenberg), 250; Introduction to Practical Chemistry for Medical, Dental and General Students (Kellas), 250; An Electric Furnace for Spectroscopic Investigations, with Results for the Spectra of Titanium and Vanadium (King), 250; Inorganic Chemistry (Kipping, Perkin), 250; Ueber die Erhaltung der Masse bei chemischen Umsetzungen (Landolt), 250; Einführung in die chemische Wissenschaft (Löb), 250; An Atlas of Absorption Spectra (Mees), 251; Ausgewählte Kapitel über Chemie (Meyer), 251; Anleitung zum zweckmässigen Rechnen bei chemischen präparativen Arbeiten (Mohr), 251; A Course in Inorganic Chemistry (Newell), 251; Die Energie. Wissen und Können (Ostwald), 251; Einführung in die Chemie (Ostwald), 251; Grundriss der Kolloidchemie (Ostwald), 251; The Fundamental Principles of Chemistry (Ostwald), 251; Elementary Modern Chemistry (Ostwald, Morse), 251; Chemistry and Literature of Beryllium (Parsons), 251; Lehrbuch der Chemie (Partheil), 252; The Romance of Modern Chemistry (Philip), 252; Die Härte der festen Körper und ihre physikalisch-chemische Bedeutung (Pöschl), 252; Die Theorie der Färbung der natürlichen Erdöle und deren notwendige Konsequenzen (Rakusin), 252; Anorganische Chemie (Remsen-Seubert), 252; Einleitung in das Studium der Chemie (Remsen-Seubert), 252; Electrochemical Investigation of Liquid Amalgams of

Thallium, Indium, Tin, Zinc, Cadmium, Lead, Copper, and Lithium (Richards, Wilson, Garrod-Thomas), 252; Exercises in Physical Chemistry (Roth), 252; Internationale Atomgewichte. Nach den Festsetzungen des internationalen Atomgewichts Ausschusses herausgegeben (Seubert), 253; Oxide of Zinc, its Nature, Properties and Uses (Smith), 253; Anorganische Chemie (Sperber), 253; Das Radium und seine Eigenschaften (Step), 253; Recent Advances in Physical and Inorganic Chemistry (Stewart), 253; Die Methoden zur Herstellung Kolloider Lösungen anorganischer Stoffe (Svedberg), 253; Physik und Chemie in gemeinverständlicher Darstellung (Weinstein), 253; Colloids and the Ultramicroscope (Zsigmondy), 254; A Text-book of Physical Chemistry: Theory and Practice (Ewell), 428; The Spectrum of Magnesium Hydride (Fowler), 428; The Periodic Law (Garrett), 428; Chemical Notes and Equations: Inorganic and Organic (Gemmell), 428; Die neueren Strahlen. Radium-Strahlen, Kathoden-, Kanal-, Anoden-, Röntgenstrahlen. In leichtfasslichen Einzeldarstellungen (Greinacher), 428; The Calculations of General Chemistry; with Definitions, Explanations, and Problems (Hale), 428; A Manual of Forensic Chemistry, Dealing Especially with Chemical Evidence, Its Preparation and Adduction (Jago), 429; Chemistry for Young People (Jenks), 429; Dispersionsmessungen an Gasen im sichtbaren und im ultraroten Spektrum (Koch), 429; Beitrag zur einer Kolloidchemie des Lebens (Liesegang), 429; A Text-book of Inorganic Chemistry (Newth), 429; Chemical Lecture Experiments (Newth), 429; An Introduction to Chemistry and Physics (Perkin, Lean), 429; Spektralanalytische und photometrische Theorien (Scheiner), 430; Ueber Elektronen (Wien), 430; Kohle und Eisen. Aus Wissenchaft und Bildung. Einzeldarstellung aus allen Gebieten des Wissens (Binz), 575; Experiments in General Inorganic Chemistry (Durkee), 575; An Introduction to Physical Science (Getman), 575; Der Verteilungssatz. Mit einer Zusammenstellung der wichtigsten Verteilungskoeffizienten zwischen flüssigen Schichten (Herz), 576; Grundlinien der Chemie für Oberrealschulen. 1 Teil: Anorganische Chemie (Rippel), 576; Die physikalischen Eigenschaften des Bodens (Trnka), 576, Crystalline Structure and Chemical Constitution (Tutton), 576; Ueber das Methangleichgewicht, die Beziehungen zwischen Nickel und Wasserstoff und einige Methansynthesen mit Calciumhydrür (Altmayer), 726; General Inorganic Chemistry (Baskerville), 726; Laboratory Exercises in Inorganic Chemistry (Baskerville), 727; Chemiker-Kalendar 1910. Hilfsbuch für Chemiker, Physiker, Mineralogen, Industrielle, Pharmazeuten, Hüttenmänner (Biedermann), 727; Physikalische Technik oder Anleitung zu Experimental-vorträgen, sowie zur Selbstherstellung einfacher Demonstrationsapparate (Frick), 727; Lernstoff aus der Physik und Chemie für Lehramtskandidaten (Gajdeczka), 727; Spektroskopie (Grebe), 727; Laboratory Exercises in General Chemistry (Kahlenberg), 727; Lehrgang der Chemie und Mineralogie für höhere Schulen (Küspert), 727; Die elektromotorischen Kräfte der Polarisation und ihre Messung mit Hilfe des Aszillographen (Le Blanc), 727; Chemie und Photographie bei Kriminalforschungen (Loock), 727; Conduction of Electricity through Gases, and Radioactivity, a Text-book with Experiments (McClung), 728; Practical Chemistry (Bruce, Harper), 813; Der Entropiesatz oder der zweite Hauptsatz der mechanischen Wärmetheorie (Hoit), 813; Photochemie (Plotnikov), 814; Einführung in die Kolloidchemie. Abriss der Kolloidchemie (Pöschl), 814; Der Aether und seine Aggregatzustande (Schmidt), 814; Neue Atomgewicht-Kurven (Wedekind, Lewis), 814; Vorlesung über Gastheorie. (2 Teile) Teil I: Theorie der Gase mit einatomigen Molekülen, deren Dimensionen gegen der mittlere Weglänge verschwinden. (2, unveränderter Abdruck) (Boltzmann), 895; Der Naturwissenschaft (Bücher), 895; Strahlungerscheinungen, Ionen, Elektronen und Radioaktivät (Bugge), 895; Lexikon der anorganischen Verbindungen (Hoffmann), 895; Trattato di chimica inorganica (Holleman), 895; Introduction to Physical Chemistry (Jones), 895; Hand und Hilfsbuch zur Ausführung physico-chemischer Messungen (Ostwald-Luther), 895; Lehrbuch der Electrochemie (Arrhenius), 1008; Die Radioaktivität (Battelli, Occhialini, Chella), 1008; Chemische Grundgesetze u Grundbegriffe, berarbeitet durch Schülerübungen (Bauckner), 1008; Synthetic Inorganic Chemistry (Blanchard), 1008; The Atmosphere, its Characteristics and Dynamics (Cordeiro), 1008; Optical Instruments Simply Explained (Davidge), 1008; Die Chemie in der Rechtspflege (Dennstedt), 1008; Handbuch der anorganischen Chemie (Gmellen, Kraut), 1009; Manipulations chimiques (Joly), 1009; Chemie des täglichen und wirtschaftlichen Lebens (Mellmann), 1009; Die Allotropie der chemischer Elemente (Meyer), 1009; Cours de chimie minérale (de Coninck), 1010; Die Schule der Physik, besonders für das Selbstudium verfasst (Oettingen), 1010; Die Schule der Chemie (Ostwald), 1010; Choix de preparations de chimie inorganique (Perkin), 1010; La materia radiante ed i raggi magnetici (Righi), 1010; Die geologischen Unterlagen des Radiums (Simmersbach), 1010; Logic of Nature (White), 1010; Grundzüge der Chemie und Mineralogie (Arendt), 1110; The Colloid Matter of Clay and its Measurement (Ashley), 1110; Radiochemistry (Cameron), 1110; A Recalculation of the Atomic Weights (Clarke), 1110; International Language and Science (Couturat, Lorenz, Ostwald), 1110; Thermodynamique et chemie (Duhem), 1110; Wie studiert man Chemie und die beschreibenden Naturwissenschaften? (Gumbrecht), 1111; Die Stromerzeugung durch fallende Teilchen in Flüssigkeiten und der absolute Nullpunkt des Potentials (Mäkelt), 1111; Platinum Resistance Thermometry at High Temperatures (Waidner, Burgess), 1112; Five-figure Logarithms and Tables for Chemists (Woodward), 1112; Fortschritte der naturwissenschaftlichen Forschung (Abderhalden), 1362; The Electron Theory (Albe), 1362; Das Wasser. Experimentalvorträge (Anselmino), 1362; Die Atmosphäre der Planeten (Arrhenius), 1363; Condensation of Vapor as Induced by Nuclei and Ions (Barus), 1363; Untersuchung über das Platin Hexabromoplatineate organischer Ammoniumbasen (Bauriedel), 1363; Ueber braunes amorphes Silicium (Benthaus), 1363; Elemente der theoretischen Physik (Christiansen, Müller), 1363; Das chemische Praktikum (Dennert), 1363, Lehrbuch der anorganischen Chemie (Erdmann), 1363, Manuel de travaux de chimie minérale (Guichard), 1364; Jahrbuch der Radioaktivität und Elektronik, 1364, Das Radium u die Erscheinungen der Radioaktivität (Kauffmann), 1364; A Manual of Chemistry, Theoretical and Practical, Inorganic and Organic (Luff, Candy), 1364; Lehrbuch der Elektrizität und des Magnetismus (Mie), 1365; Oil: Animal, Vegetable, Essential and Mineral (Mitchell), 1365, Grundriss der anorgan. Chemie (Oppenheimer), 1365; Ueber Katalyse (Ostwald), 1365; Die Brownsche Bewegung u. die wahre Existenz der Molekule (Perrin), 1365, Radioactivity of the Thermal Waters of Yellowstone National Park (Schlundt, Moore), 1365, Atomauflosung u. elektromotorische Kraft (Schmidt), 1365, Mathematical and Physical Papers Bd IV Hydrodynamics and General Dynamics (Thomson), 1366, Contribution a l'étude de l'azoture d'aluminium et de l'azoture de baryum (Wolk), 1366; Nouvelles manipulations de chimie (Blouet), 1537; Traité de physique (Chowlson), 1537; Water, its Origin and Use (Coles-Finch), 1537; On Scandium (Crookes), 1537; Untersuchungen über die bei der Elektrolyse von Nickelsalzen auftretenden periodischen Erscheinungen (Dietrich), 1537, Principles of Chemical Geology (Elsden), 1537, La physico-chimie (Fauvelle), 1537, A High School Course in Physics (Garton), 1537; Spark Spectra of the Metals (Gissing), 1537, Rayons X et radiations diverses (Guilleminot), 1537; Viskosität binärer Flussigkeitsgemische (Kassel), 1538; Der Radiumvorrat der Natur (Kurz), 1538, Nouvelle théorie des sciences physiques. Unité de la matière, étude des fluides, force, travail, energies rayonnantes, électricité (Lachaud), 1538; Radium (Lord), 1538; Ueber Hydrate, deren Dampfspannung sich kontinuierlich mit der Zusammensetzung ändert (Löwenstein), 1538, Popularwissenschaftliche Vorlesungen (Mach), 1538, Ueber die Bildung von Legierungen durch Druck und über die Reaktionsfähigkeit der Metalle im festen Zustande (Masing), 1538; Les états physiques de la matière (Maurain), 1538, Versuch einer chemischen Auffassung des Weltäthers (Wendeléff), 1538; Die Materie der chemischen Elemente und das Wesen der chemischen Reaction (Meusel), 1538, A Manual of Elementary Practical Chemistry (Oscroft, Shea), 1539; Die Forderung des Tages (Ostwald), 1539, La matière, l'éther, l'électricité (Proumen), 1539; Lehrbuch der anorganischen Chemie (Richter), 1539, Anorganisch-chemisches Praktikum Qualitative Analyse und anorganische Präparate (Riesenfeld), 1539, Chemie (Rivals, Devaud), 1539; The Relations between Chemical Constitution and Some Physical Properties (Smiles), 1539; Ueber die Radioaktivitätsverhältnisse der natürlichen Heilquellen des Deutschen Sprachgebietes (Sommer), 1539, The Theory and Ionization of Gases by Collision (Townsend), 1540; International Catalogue of Scientific Literature, 1698; Anleitung zur Darstellung chemischer anorganischer Praparate (Blochmann), 1698; Ueber Radiumforschung (Exner), 1698; Lehrbuch der anorganischen Chemie (Holleman), 1698, Sammlung chemischer und chemisch-technischer Vorträge (Herz), 1698, A First Year's Course of Inorganic Chemistry (Hood), 1698; Handbuch der Spektroskopie (Kayser), 1699; Leitfaden der graphischen Chemie. Erläuterung einiger wichtiger Schulbeispiele (Kremann), 1699; Ueber Aether und Materie (Lenard), 1699; Ueber Synthese des Ammoniaks aus den Elementen (Lipski), 1699, Ueber die Reaktion zwischen Sulfuryl chlorid und Ammoniak (Michel), 1699; The Elements (Tilden), 1699; Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge (Walden), 1700; Essentials of Chemistry (Williams). 1700

Analytical: Anleitung zur quantitativen chemischen Analyse (Hlasiwetz), 249; Uebungen in quantitativen chemischen Analyse (Fichter), 249, Ueber den Ersatz des Schwefelwasserstoffs in der qualitativen chemischen Analyse (Donath), 248; Massanalyse (Crato), 248; Quantitative Chemical Analysis (Clowes, Coleman), 248, Systematic Qualitative Analysis for Students of Inorganic Chemistry (Caven), 248; Leitfaden der chem. Analyse (Birnbaum), 248; Qualitative Analyse anorganischer Substanzen (Biltz), 247; Kolorimetric und quantitative Spektralanalyse in ihrer Anwendung in der Chemie (Krüss, G. and H.), 250; Beiträge zur mikrochemischen Analyse (Schoorl), 252; Wie scheidet man Nickel am besten ab auf elektrolyt. Weg? (Schumann), 252, Einführung in die qualitative chemische Analyse zum Gebrauch bei den prakt. Uebungen im Laboratorium (Wiechowski), 253; Beilsteins Anleitung zur qualitativen Analyse (Winterstein, Trier), 254; Chemisches Praktikum (qualitative Analyse) für höhere Lehranstalten (Wolland), 254; Outlines of Qualitative Chemical Analysis (Gooch, Browning), 428; A Manual of Qualitative Chemical Analysis (McGregory), 429; Die Bestimmungsmethoden des Wismuts und seine Trennung von den

Anderen Elementen (Moser), 429; An Elementary Treatise on Qualitative Chemical Analysis (Sellers), 430; Praktikum der quantitativen anorganischen Analyse (Stock, Stähler), 430; La réfractométrie et ses applications pratiques (Sidersky), 576; Commercial Organic Analysis (Allen), 726; Manuel théorique et pratique d'analyse volumetrique (Duparc, Basadonna), 727; Anleitung zur organischen Elementaranalyse (Henle), 727; Chemisch-technische Untersuchungsmethoden (Lunge, Berl), 728; Uebungsbeispiele zur quantitativen Analyse (Meigen), 728; Anleitung zur quantitativen chemischen Gewichtsanalyse nach C. Zimmermann (Pechmann), 1010; Die Methoden der Massanalyse (Beckurts), 1110; Theoretical Principles of the Methods of Analytical Chemistry Based upon Chemical Reactions (Chesneau), 1110; Qualitative Analysis, Tables for Use at the Bench (Lewis), 1111; Quantitative Analysis (Treadwell), 1112; Qualitative Chemical Analysis, Organic and Inorganic (Perkin), 1365; Uebungsbeispiele aus der quant. chem. Analyse (Vortmann), 1366; Tabellen zur chemischen Analyse (Wallach), 1366; Anleitung zur vereinfachten Elementaranalyse für wissenschaftliche und technische Zwecke (Dennstedt), 1537; Einleitung in die Chemische Analyse (Medicus), 1538; Lötrohrprobierkunde (Henglein), 1698; A Manual for Assayers and Chemists (Seamon), 1699; La réfractométrie et ses applications pratiques (Sidersky).. 1699

Organic: Ueber das Verhalten einiger aromatischer Essigsäure- und Glykollderivate tierischen Fermenten gegenüber (Minkowski), 251; Die orientierenden Einflüsse und der Benzolkern (Obermiller), 251; Formaldehyd (Orloff), 251; Introduction to the Preparation of Organic Compounds (Fischer), 428; Modern Organic Chemistry (Keane), 429; Contributions à la connaissance des oxyaldéhydes orthovanilline et l'aldehyde orthovératrique (Noelting), 429; Die Sulfosäuren des Anthrachinons und seiner Derivate (Goldberg, Friedmann), 576; Ueber α-Oxolaktame (Roschke), 576; Die Knallsäure (Wieland) 576; Ueber Oxalmalonsäureester (Heuser), 727; Systematic Practical Organic Chemistry (Norman), 728; Ueber Konstitution und Farbe der Chinonimine (Piccard), 728; An Introduction to the Study of Compounds of Carbon (Remsen), 728; Ueber die Bildung der Naphthene im Erdöl (Routala), 728; Ueber Synthesen ringförmiger Verbindungen mittels Dipropylmalonylchlorids und Succinylchlorids (Rothschild), 728; Practical Organic Chemistry (Sudborough, Campbell), 728, The Simple Carbohydrates and the Glucosides (Armstrong), 813; Einfluss der Lösungsmittel auf die Verteilung der Isomeren (Bruner, Vorbrodt), 813; Sur une association naturelle de dimethylanthracènes (Lavaux), 813; Les synthèses dans le groupe de l'indigo (Pozzi-Escot), 895; Untersuchungen über die Affinitäten. Ueber Bildung und Zersetzung der Aether (Berthelot, Péau de Saint-Gilles), 1008; Methoden der Organischen Chemie, 1009; Cours de chimie organique et biologique (Porcher, Nicolas), 1010; Jahrbuch der Organischen chemie (Schmidt), 1010; Die direkte Einführung von Substituenten in den Benzolkern (Holleman), 1111; Organische Chemie und die Lehre vom Leben (Wohl), 1112; Lehrbuch der organischen Chemie (Holleman), 1364; Ueber Nitrocumarine und ihre Konstitutionsermittelung (Landsberger), 1364; Outlines of Organic Chemistry (Moore), 1365; Die elektrolytischen Prozesse der organischen Chemie (Moser), 1365; A Method for the Identification of Pure Organic Compounds. Vol. 3. Identification of the Commercial Dyestuffs (Mulliken), 1365; Studien über Konstitutionsermittelung monohalogenisierter, mono- und dialkylierter Monoketone der Cyclohexanreihe (Steinhorst), 1366; L'acide thyminique (Duhamel), 1537; Elektrische Doppelbrechung der Kohlenstoffverbindungen (Leiser), 1538; Die Cellulose (Piest), 1539; Abbau des Morphobetains, II. Ueber einige Additionsprodukte cyclischer Basen mit Hydrochinon (Rettberg), 1539; Lexikon der Kohlenstoffverbindungen (Richter), 1539; Ueber die Reduktion von Pinen zu Pinan; Eigenschaften und chem. Verhalten des letzteren (Schenk), 1540; Die Alkaloide; eine Monographie der natürlichen Basen (Winterstein, Trier), 1540; Notions fondamentales de chimie organique (Moureu).............. 1699

Biological, Pharmaceutical and Foods: Bakteriologisches Taschenbuch, enthaltend die wichtigsten technischen Vorschriften zur bakteriologischen Laboratoriumsarbeit (Abel), 247; Die Auffindung der Gifte und stark wirkender Arzneistoffe (Autenrieth), 247; Elementary Photomicrography (Bagshaw), 247; Grundlagen und Ergebnisse der Pflanzenchemie (Euler), 248; Lehrbuch der Chemie für Pharmazeuten (Fischer), 249; Lehrbuch der chemischen Toxikologie und Anleitung zur Ausmittelung der Gifte, für Chemiker, Apotheker und Mediziner (Gadamer), 249; Repetitorium der pharmazeutischen Chemie (Gerke), 249; Biochemisches Taschenbuch (Glikin), 249; Der Tafelsenf (Mostrich) und die technische Verwertung der Senfpflanze (Hasterlik), 249; Lehrbuch der Pharmakognosie (Karsten, Oltamus), 250; Praktikum der Bakteriologie und Protozoologie (Kirskalt, Hartmann), 250, Analytisches Diagnostikum. Die chemischen mikroskopischen und bakteriologischen Untersuchungsmethoden von Harn, Auswurf, Magensaft, Blut, Kot (Kraft), 250; Phenol und seine Derivate als Desinfektionsmittel (Laubenheimer), 250; Die Beziehungen der Chemie zur Biologie und Medizin (Lockemann), 250; Dynamik der Oberflächen. Eine Einführung in biologische Oberflächenstudien (Michaelis), 251; Aids to the Analysis of Food and Drugs (Moor, Partridge), 251; Grundriss der Pharmakochemie (Oesterle), 251; Die Fermente und ihre Wirkungen (Oppenheimer), 251; The Vegetable Proteins (Osborn), 251; Lehrbuch der Pharmakologie (Poulsson), 252; Grundriss der Pharmakologie in Bezug auf Arzneimittellehre und Toxikologie (Schmiederberg), 252; Chemische Konstitution und physiologische Wirkung (Spiegel), 253; Methoden zur Untersuchung von Milch und Molkereiprodukten (Teichert), 253; Praktische Anleitung zur Ausführung des biologischen Eiweissdifferenzierungsverfahrens mit besonderer Berücksichtigung der forensischen Blut- und Fleischuntersuchung, sowie der Gewinnung präzipitierender Sera (Uhlenhuth, Weidanz), 253; Untersuchungen über "Antiformin," ein bakterienauflosendes Desinfektionsmittel (Uhlenhuth), 253; Spices and How to Know Them (Gibbs), 428; Die Bakteriologie des täglichen Lebens (Jaeger), 429; Ueber die chemische Durchlässigkeitlebender Algen- und Protozoenzellen für anorganische Salze und die spezifische Wirkung letzterer (Mengarini, Traube, Scala), 429; Selbstbereitung pharmazeutischer Spezialitäten (Mindes), 429; Schadliche Nebenwirkungen der Arzneimittel (Paczkowski), 429; Beiträge zur Photographie der Blutspektra unter Berücksichtigung der Toxikologie der Ameisensäure (Rost, Heise), 429; Die Erkennung von Blutflecken und die Unterscheidung von Menschen- und Tierblut in der Gerichtspraxis, zugleich eine Schilderung der Haupteigenschaften des Blutes, sowie der Blutverwandtschaft unter den Tieren (Schmidt), 430; Klinische Spektroskopie (Schumm), 430; Elements de chimie génerale, préparatoires à l'études biochimique des fermentations (Vandevelde), 430; Praktische Pharmazie (Fernau), 575; Physiologische Wirkungen der Benzoesaüre und des benzoesäüren Natrons (Gerlach), 575, Food Inspection and Analysis (Leach), 576; Handbuch der biochemischen Arbeitsmethoden (Abderhalden), 726, Outlines of Bacteriology (Ellis), 727; Ueber Vorkommen und Herkunft des Inosit im Tierkörper (Klein), 727; Chemie der Menschlichen Nahrungs- und Genussmittel (König), 727; Food Inspection. A Practical Handbook (MacEwen), 728; Handbuch der Biochemie der Menschen und der Tiere II Bd. 2 Hälfte: Biochemie der Gewebe und Organe (Oppenheimer), 728; Chemisches Praktikum für Mediziner (Rimbach), 728; The Proteins (Robertson), 728, Die Giftprüfung und die Konzession zum Handel mit Giften (Syllwaschy), 728; Lehrbuch der physiologischen Chemie (Hammarsten), 813; Les ferments protéolytiques Etude chimique et pharmacotechnique (Javillier), 813; Flüssige Krystalle, Myelinformen und Muskelkraft (Lehmann), 814; Toxikologische Chemie (Mannheim), 814; Beitrage zur Biochemie des Bodens (Moll), 814; Leitfaden der Milchhygiene (Schlossmann), 814; Conférences de pharmacie, Tome 4. Analyses d'urines, de fèces, de lait (Battegay), 895; Fabrication du chocolat (Fritsch), 895; Handbuch der biochemischen Arbeitsmethoden (Abderhalden), 895; Questions and Answers on Milk Testing (Publow, Troy), 895; Lehrbuch der Nahrungsmittelchemie (Röttger), 896; L'ambiente chimico ed i fermenti selezionati (Soucini), 896, Milch und Molkereiprodukte; ihre Eigenschaften, Zusammensetzung und Gewinnung (Sommerfeld), 896; Précis de chemie physiologique (Arthus), 1008; Il trattamento naturale ed artificiale delle acque da fogna, secondo i moderni sistemi di epurazione biologica (Ferrari), 1009; Chemische Untersuchung der Georgen-, Marien-, Wiesen-, Mariannen- und Friedrichs-Quelle zu Bad Landeck (Fresenius), 1009; Lehrbuch der Pharmakognosie (Gilg), 1009; Lehrbuch der physiologischen Chemie (Hammarsten), 1009, Die menschlichen Genussmittel, ihre Herkunft, Verbreitung, Geschichte, Bestandteile, Anwendung und Wirkung (Hartwig), 1009; Fleischvergiftungen und Paratyphusinfektionen, ihre Entstehung und Verhütung (Hübener), 1009; Die experimentelle Pharmakologie als Grundlage der Arzneibehandlung (Meyer, Gottlieb), 1009; Tossicologia forense (Muccioli), 1009; Nahrungsmittel-Chemie (Rottger), 1010; Lehrbuch der Physiologie des Menschen (Tigerstedt), 1010, Handbuch der Pharmakognosie (Tschirch), 1010; Methods Used in the Examination of Milk and Dairy Products (Barthel), 1110; Mikrophotographischer Wandatlas der Bakteriologie (Bujwid), 1110, Ergänzungstaxe zur Deutschen Arzneitaxe für 1910, 1110; Algemeine Chemie der Enzyme (Euler), 1110; Fermentazione e fermenti (Guareschi), 1111; Pharmazeutisch-technisches Manuale (Hell), 1111; Real-Enzyklopädie der gesamten Pharmazie (Moeller, Geisler), 1111; Analyse und Antidote der für den Arzt wichtigsten Gifte (Neumann), 1111; Arzneiverordnungen 1910. Die neuesten Arzneimittel und Spezialitäten (Rabow), 1111; Manual of Medical Jurisprudence, Toxicology and Health (Robertson), 1112; Hefen, Schimmelpilze und Bakterien (Bersch), 1363; Revue des médicaments nouveaux et de quelques médications nouvelles (Crinon), 1363; La chimie de matière vivante (Duclaux), 1363; Kurzgefasste Anleitung zu den wichtigeren hygienischen Untersuchungen (Fischer), 1363; Lehrbuch der Toxikologie für Tierärzte (Fröhner), 1363; Dealin, ein neues Antiseptikum (Hancken), 1364; Botanisch-mikroskopisches Praktikum (Kienitz-Gerloff), 1364; Die Fabrikation des Surrogatkaffees und des Tafelsenfes (Lehmann), 1364; Beitrag zur Kenntniss der Wirkung der Formaethrolpräparate (Liess), 1364; Examination of Water (Chemical and Bacteriological) (Mason), 1364; Die Untersuchung und Beurteilung des Wassers und des Abwassers (Ohlmüller, Spitta), 1365; Laboratory Notes on Industrial Water Analysis (Richards), 1365; Introduction to the Analysis of Drugs and Medicines (Nelson), 1365; Air, Water, and Food from a

Sanitary Standpoint (Richards, Woodman), 1365; Lehrbuch der Arzneimittellehre und Arzneiverordnungslehre (Tappeiner), 1366; The Compendium of Medicine and Pharmacy (Thompson), 1366; Nach Autoren und Sachnamen geordnete Sammlung der wichtigsten Reagenzien und Reaktionen für Chemie, Pharmazie, Physiologie usw. (Waldheim), 1366; Nouveaux éléments de pharmacie (Andouard), 1536; Elemente der physiologischen Chemie (Arthus), 1536; Das Wesen der Enzymwirkung (Bayliss), 1536; Guide pour les manipulations de chimie biologique (Bertrand, Thomas), 1537; Recherches sur l'épuration biologique et chimique des eaux d'égout (Calmette), 1537; Vergiftungen, Klinischen Teil. 2 Hälfte: Die organischen Gifte (Erben), 1537; Chemie und Physiologie der Milch (Grimmer), 1537, Die Vergiftungen (Jaksch), 1537; Die Arzneitherapie der Gegenwart (Kahane), 1538; Ueber das Wesen der Alkoholgärung (Kohl), 1538, Hilfstabelle für Nahrungsmittelchemiker (Kraus, Schwenzer), 1538; Mikroskopie und Chemie am Krankenbett (Lenhartz), 1538; Zur Frage von dem Einfluss der Milchnahrung auf den Stickstoff und Phosphorumsatz (Minz), 1538; Die Eisenbakterien (Molisch), 1538; Buchheisters Vorschriftenbuch für Drogisten (Ottersbach), 1539; Physical Chemistry, its Bearing on Biology and Medicine (Philip), 1539; Practical Sanitation (Reid), 1539; Ueber Bestimmungsmethoden der Cellulose (Renker), 1539; Handbuch der Milchkunde (Rievel), 1539; Kursus der physiologischen Chemie mit Anleitung zur qualitativen und quantitativen Analyse des Harns (Rosanow), 1539; Lehrbuch der pharmazeutischen Chemie. Teil I· Anorganischer Teil (Scholtz), 1539; Methoden der chemische en microscopische Diagnostick (Steensma), 1539; Cours de chimie physiologique et pathologique (Strzyzowski), 1540; Arbeiten aus dem pharmazeutischen Institut der Universität Berlin (Thoms), 1540; Ueber das Verhalten der Alkaloide in den Organen der Atropa belladonna L (Trögele), 1540, Contribution a la connaissance de divers phénomènes oxydasiques naturels et artificiels (Wolff), 1540; Ueber die Bindung der Derivate des Jods an das Gewebe der Leber (Wyssozky), 1540; Handbuch der Biochemie des Menschen und der Tiere, 1698;
Atlas der Krystallformen und der Absorptionsbänder der Hämochromogene (Dilling), 1698
Organanalytische Untersuchungen über dem Stickstoff- u. Phosphorstoffwechsel u. ihre gegenseitigen Beziehungen (Grund), 1698, Bakteriologisch-chemisches Praktikum (Prescher, Rabs) 1699

Metallurgical and Mineralogical: Die binären Metallegierungen (Bornemann), 248; Der basische Herdofenprozess (Dichmann), 248; Spezialstähle in Theorie und Praxis (Giesen), 249; La métallurgie électrique (Graffigny), 249, The Theory and Practice of Enamelling on Iron and Steel (Grünwald), 249; Metallographie (Guertler), 249; Igneous Rocks (Iddings), 249; Laboratory Notes on Iron and Steel Analysis (Macfarlane), 250, The Recognition of Minerals (Moor), 251; Eisenreduktion in Puddelofen (Otto), 251; Die Herstellung von hochprozentigen Ferrosilicium im elektrischen Ofen (Pick, Conrad), 252; Zink, Zinn, und Blei (Richter), 252; Tabellen zur Bestimmung der Mineralien mittels ausserer Kennzeichen (Weisbach), 253; The Metallurgy of Common Metals, Gold, Silver, Iron, Copper, Lead and Zinc (Austin), 428, Gold Refining (Clark), 428; Die Legierungen (Fermum), 428; Analyse des métaux par electrolyse. Métaux industriels; alliages, minerals, produits d'usines (Hollard), 429, Summary of Alloys (Jänecke), 429; Technical Methods of Ore Analysis (Low), 429; Blast Furnace Practice (Morgan), 429; The Elements of Metallography (Ruer), 430; Hints on Amalgamation and the General Care of Gold Mills (Adams), 575; Industries du plomb et du mercure. Bd. I. Métallurgie (Bouchonnet), 575; Die Metallhüttenchemie (Orthey), 576; Crystallography: An Elementary Manual for the Laboratory (Wadsworth), 576; Text-Book of Ore Dressing (Richards), 728; Fuel and Refractory Materials (Sexton), 728; The Chemistry of Cyanide Solutions Resulting from the Treatment of Ores (Clennell), 813; Die physikalisch-chemischen Eigenschaften der Legierungen (Dessau), 813; Analyse thermique et métallographie microscopique (Rengade), 814; The Corrosion of Iron and Steel (Sang), 814; Book of Precious Stones. Identification of Gems and Gem Minerals and Account of their Scientific, Commercial and Artistic Aspects (Wodiska), 814; Analyse der Silicat- und Carbonatgesteine (Hillebrand), 895; Industrie du chrome, du manganèse, du nickel et du cobalt (Ouvrard), 895; La soudure autogène des métaux (Ragno), 895; Analyse thermique et métallographie microscopique (Rengade), 896; Zur chemisch-mineralogischen Erforschung der Deutschen Kalisalzlagerstätten (Rinne), 896; Leitfaden der Mineralogie (Ruska), 896; Metallography (Desch), 1008; Treatise on Ore and Stone Mining (Foster), 1009; Kurze Uebersicht über sämtliche Legierungen (Jänecke), 1009; Metallography Applied to Siderurgic Products (Savoia), 1010; Hüttenmännische Probierkunde (Schütz), 1010; Mitteilungen aus dem eisenhüttenmännischen Institut der Kgl. Techn. Hochschule Aachen (Wüst), 1010; Dictionary of Portuguese Mining Terms, with French, English, and German Equivalents (Ackermann), 1110; The Corrosion and Preservation of Iron and Steel (Cushman, Gardner), 1110; Ore Deposits of South Africa (Johnson), 1111; Manual of the Chemical Analysis of Rocks (Washington), 1112; Bleiraffination durch Elektrolyse (Betts), 1363; Die Metallfärbung (Buchner), 1363; Lead Smelting (Collis), 1363; A Reconnaissance of the Gypsum

Deposits of California (Fess, Steyer), 1363; Die synthetischen Edelsteine (Grossmann, Neuburger), 1363; The Mercury Minerals from Terlingua, Texas (Hillebrand, Schaller), 1364; Handbuch der Mineralogie (Hintze), 1364; Durchführung des Roheisen-Erz Prozesses im Martinofen (Kahnert), 1364, Handb. der autogenen Schweissung (Kautny), 1364; Beiträge zur Ezaufbereitung (Lukaszczyk), 1364, Modern Foundry Practice (Sharp), 1365; Modern Assaying (Smith), 1365, Taschenbuch für Eisenhüttenleute, 1366, Beiträge zur Oxydation des Phosphors im basischen Konverter (Voigt), 1366; La néo-métallurgie, ses moyens et ses methodes (Benolt), 1537; Neue massanalytische Methoden zur Bestimmung von Eisen und Blei (Bollenbach), 1537, Etude sur la corrosion des métaux (Buzenac), 1537; Essais des fers et des aciers par corrosion (Frémont), 1537; Iron-ore Resources of the World, 1537; Studien über die Zusammensetzung heliumführender Mineralien (Lange), 1538; Note sur la fabrication électrolytique de l'aluminium (Lodin), 1538; A Treatise on Electrometallurgy (McMillan), 1538; Précis de métallurgie (Pécheux), 1539, Ueber die binären Systeme des Natriummetasilicats mit Lithium-, Magnesium , Calcium-, Strontium-, und Bariummetasilicat (Wallace), 1540; Der praktische Hochofenbetrieb (Bender), 1698; Mineralogia descrittiva (Bombici), 1698; Mitteilungen aus dem Institut fur Metallographie und Probierkunde an der kgl. sächs. Bergakademie Freiberg (Friedrich), 1698; The Cupola Furnace (Kirk), 1699; Die Untersuchungsmethoden des Eisens und Stahls (Rüdisüle)............ . . 1699

Photography: Die Herstellung von Diapositiven (Hanneke), 249, Optisches Hilfsbuch für Photographierende (Harting), 249, Vergrössern und Kopieren auf Bromsilberpapier (Löscher), 250; Die photographische Praxis (Schmidt), 252, Photographie (Vogel), 253, Taschenbuch der Photographie Ein Leitfaden für Anfänger und Fortgeschrittene (Vogel), 253; Photographisches Reisehandbuch (Wentzel, Paech), 253; Ueber Farbenphotographie und verwandte naturwissenschaftliche Fragen (Wiener), 254; Photography in Principle and Practice (Bottomley), 428, The American Annual of Photography (Tennant), 430; Wie erlangt man brillante Negative und schöne Abdrucke (Hauberrisser), 727; Traité pratique de photographie des couleurs (Niewenglowski), 895, Le diamidophenol acide en photographie (Underberg), 896, Lexikon für Photographie u Reproduktionstechnik (Emmerich), 1008, Kaufmännisches Handbuch des Photographen (Frank), 1363, Chemistry for Photographers (Townsend). 1699

Agricultural: Fabrikation des engrais chimiques (Fritsch), 249; Fertilizers and Manures (Hall), 249; Das Kalisilicat (Phonolithmehl) als Kalidüngemittel (Wein), 253, Mineralische Düngemittel u Ernteergebnisse (Schneider), 430, Kleines Handwörterbuch der Agrikulturchemie (Passon), 728; Kleines Handwörterbuch der Agrikulturchemie (Passon), 895; Soil Fertility and Permanent Agriculture (Hopkins), 1111, Die Kalk- und Magnesiadungung (Meyer), 1111; Fertilizers and Feeding Stuffs (Dyer), 1363, Chemie und landwirtschaftl Nebengewerbe (Meyer), 1365, Soils and Manures (Murray), 1365; Die Kalidüngung (Schneidewind), 1365; Düngerlehre (Stutzer), 1366, Agricultural Bacteriology, Theoretical and Practical (Percival), 1539; Fertilizers for Wheat Soils (Whitney) 1540

Fermentation Die Mikroörganismen der Gärungsindustrie (Jörgensen), 250; Leitfaden der Chemie für Brauer und Mälzer (Knorr), 250; Die Spiritusindustrie, ihre Technik, Steuern und Monopole (Linschmann), 250, Composition chimique des alcools d'industrie et des spiritueux (Moraucé), 251, Zuckerungstabellen zur gesetzlich erlaubten Verbesserung der Traubensäfte, und Weine, sowie der Obst- und Beerensäfte (Schätzlein), 430, Tabellen zur Ermittelung der freien Saüre, sowie der flüchtigen und nichtflüchtigen Saüren im Wein (Friese), 575; Praktische Destillateur-Kursus (Goettler), 576, Tafel zur Umrechnung der Volumprozente in Gewichtsprozente und der Gewichtsprozente in Volumprozente bei Branntweinen, berechnet nach den amtlichen Zahlen der kaiserlichen Normal-Eichungskommission (Plato), 576; La chimie et la bactèriologie du brasseur Hannut. (Flamand), 727; Bierbrauerei (Codounsky), 1008; Contribution a l'analyse physico-chimique des vins (Duboux), 1008; Die Malz- und Bierbereitung (Leyser), 1009; Praktische Mälzerei-und Brauerei-Betriebskoturolle (Schifferers), 1010; Distillazione del vino ed utilizzazione dei residui della vinificazione (Cettolini), 1110; Dal mosto al vino La fermentazione alcoolica, 1110; Illustriertes Brauerei-Lexikon (Delbruck), 1537; Atlas der mikroskopischen Grundlagen der Gärungskunde (Lindner), 1538; Utilisation des sous-produits de la vigne et du vin (Vermorel, Dantony) . 1699

Essential Oils Ueber die Entwickelung der Industrie der aetherischen Ole in den letzten 25 Jahren (Hesse), 428; Die moderne Parfümerie (Mann), 728, Laboratoriumsbuch für die Industrie der Riechstoffe (Simon), 728; Die ätherischen Oele Monographien über chemisch-technische Fabrikationsmethoden (Leimbach), 1364; Theorie der Gewinnung und Trennung der ätherischen Oele durch Destillation (Rechenberg).......... 1539

Acids, Alkalies and Salts: Die Fixierung des Luftstickstoffs und ihre Bedeutung für Ackerbau und Industrie (Erdmann), 248; Ueber die Darstellung des Chlorkaliums aus Hartsalz (Felb), 248; La fabrication électrochimique de l'acide nitrique et des composés nitrés à l'aide des éléments de l'air (Escard), 428; Fertilizer and Acid Plants (MacKnight), 429; Ueber die

Darstellung des Chlorkaliums aus Hartsalz (Feit), 575; The Manufacture of Sulphuric Acid and Alkali, with the Collateral Branches (Lunge), 576; Die Stickoxybildung aus Luft mit Hilfe einer Gleichstromentladung niedriger Spannung unter vermindertem Druck (Morden), 728; Ueber Luftsalpeter (Jurisch), 813; Die Gewinnung des Broms in der Kaliindustrie (Mitreiter), 814; Industries des acides minéraux. Acides sulfurique, chlorhydrique et azotique (Band), 894; La soude électrolytique (Brochet), 1363; Gesetz über Absatz von Kalisalzen vom 23 Mai 1910 (Silberberg), 1699; Illustr. Jahrbuch der Wirtschaft und Technik im deutschen Kalisalzbergbau, nebst Richskaligesetz mit einer krit. Einleitung (Stange).......... 1699

Glass and Ceramics: Glasätzerei (Miller), 251; History of the Clay-working Industry in the United States (Ries), 252, Einfaches chemisches Praktikum für Keramiker, Glastechnike, Metalltechniker usw. (Berdel), 428; Keramik (Rudolph), 430; Steingutfabrikation (Heim), 813; Porzellan (Ricke), 814; Aus der Praxis eines Glashüttenfachmannes (Schippman), 814; Die Tonwarenerzeugung, mit besonderer Berücksichtgung der chemischen Grundlagen (Rudolf), 1010; Photokeramik (Fleck), 1111; Die Bayerische Spiegelglasindustrie (Berlin), 1363; Der elektrische Ofen im Dienste der keramischen Industrie (Brown), 1363; La technique de l'émaillerie moderne (Grunwald), 1364; Laboratoriumsbuch für die Tonindustrie (Bollenbach), 1537; La céramique française (Peyre), 1539; Das Porzellan (Rieke).......... 1699

Cement: Portland Cement (Davis), 248; Der Erhärtungsprozess der Kalkhaltigen hydraulischen Bindemittel (Michaelissen), 251; Hydraulischer Kalk und Portlandzement, ihre Rohstoffe, physikalischen und chemischen Eigenschaften (Zwick), 254; Der Eisenbetonbau (Haimovici), 576; Anleitung zum Entwerfen und zur Berechnung der Standfestigkeit von Fabrikschornsteinen aus Mauerwerk, Eisen und Eisenbeton, nebst den hierüber erlassen Bestimmungen und die rauchfreie Verbrennung bei Dampfkesseln (Jahr), 576; Cement in Sea Water (Poulsen), 576; Zement im Meerwasser (Poulien), 814; Cement and How to Use it (Radford), 1111; Laboratoriumsbuch für die Zementindustries (v. Arlt), 1362; Zentralblatt für Chemie und Analyse der hydraulischen Zemente.......... 1366

Fuels and Lighting: Torfkoks und Kraftgas (Jabs), 250; Die flüssigen Heizmaterialien und ihre Anwendung (Rossmässler), 252; Les combustions industrielles Le controle chimique de la combustion (Rousset, Henri, Chaplet), 252; Kokerei und Teerprodukte der Steinkohle (Spilker), 253; Commercial Peat; Its Uses and Possibilities (Gissing), 428; Coal Tar and Ammonia (Lunge), 576; Modern Coking Practice; Including the Analysis of Materials and Products (Byrom, Christopher), 727; Ueber Gasöle und Oelgas (Hempel), 727; Acetylene: The Principles of Its Generation and Use (Leeds, Butterfield), 727; Rechentafeln für Beleuchtungstechniker (Bertelsmann), 813; American Producer Gas Practice and Industrial Gas Engineering (Latta), 813; Vorlesungen über Brennstoffkunde (Aufhäuser), 894; Illumination and Photometry (Wickenden), 896; Einrichtung und Betrieb eines Gaswerkes (Schäfer), 1010; Theorie und Praxis des Generatorbetriebes (Waldeck), 1010; Das Generatorgas, seine Erzeugung und Verwendung (Kietaibi), 1111; Betriebsbuchfuhrung für Gaswerksbetriebe (Greineder), 1363; Die Oelfeuerung im Schmiedebetrieb und im der Metalwarenfabrikation (Pick), 1365; L'éclairage industriel (Berthier), 1537; Die Technik der Verbrennung und Energiegewinnung aus städtischen Abfallstoffen (Meyer), 1538; Ueber ökonomischen Kohlenverbrauch (Parma).......... 1359

Petroleum and Asphalt: Erdwachs, Paraffin, und Montanwachs, deren Darstellung und Verwendung (Gregorius), 428; Untersuchung der Mineralöle und Fette, sowie der ihnen verwandten Stoffe (Holde), 428; Solid Bitumens (Peckham), 576; Fabrication des huiles minérales et pyrogénées (Ehrsam), 813; Oil (Mitchell), 1538; Ueber Asphalt- und verwandte Industrien (Weil).......... 1540

Paper: Die wirtschaftliche Bedeutung der techn. Entwicklung in der Papierfabrikation (Schaefer), 252; Kurzes Lehrbuch der Chemie für Papiertechniker (Skark).......... 1365

Explosives: Die Sprengstoffe. Darstellg. u. Untersuchg. der Sprengstoffe u. Schiesspulver (Kedesdy), 250; Die Ammonsalpetersprengstoffe (Escales), 428; Die Sprengstoffe, ihrer Chemie und Technologie (Biedermann), 1110; Les explosifs militaires violents (Macar, Dalattre), 1364; Annual Report of His Majesty's Inspectors of Explosives, 1698; Chloratsprengstoffe (Escales).......... 1698

Dyes and Textils: The Practical Dry Cleaner, Scourer and Garment Dyer (Baird), 247; Les succédanés de la soie. Les soies artificielles (Chaplet, Rousset), 248; Der Indigo und seine Konkurrenten (Felsen), 248; Lehrbuch der Farbenfabrikation (Gentele), 249; Handbuch der Farbenfabrikation (Zerr, Rübencamp), 254; Die volkswirtschaftliche Bedeutung des künstlichen Indigos (Jenke), 576; Mikrophotographischer Atlas der industriellen Faserstoffe (Zetzsche), 576; A Manual of Dyeing (Knecht), 727; A Course in Dyeing for Garment Dyers (Prag), 728; La soie artificielle et sa fabrication (Foltzer), 895; Ramie China Grass (Carter), 1008; Die Theorie des Färbeprozesses (Pelet-Jolivet), 1010; Chemische Technologie der Gespinstfasern, ihre Geschichte, Gewinnung, Verarbeitung und Veredlung (Witt, Lehmann),

1010; Dyeing and Cleaning (Farrell), 1111; Das Färben und Bleichen von Baumwolle, Seide, Leinen, Etc. (Herzfeld), 1111; Der Farberlehrling im Chemie Examen (Kielmeyer), 1364; Moderne Batistfarben (Zimmermann), 1366; Anleitung zur Unterscheidung von Textilmaterialen (Hünlich), 1537; Guide pratique de teinture moderne, suivi de l'art du teinturier dégraisseur (Thomas), 1540; Les succédanés de la soie (Chaplet, Rousset), 1698; Die Chemie der Cellulose, unter besonderer Berücksichtigung der Textil- u. Zellstoffindustrien (Schwalbe).... 1699

Paints and Varnish: Oelfarbe und Oelfarbenanstriche (Hebing), 249; Couleurs, peintures et vernis (Desalme, Pierron), 895; Linseed Oil and Other Seed Oils (Ennis), 895; An Introduction to the Chemistry of Paints, with Diagrams (Friend), 1537; Handbuch der Lach- und Firnis-Industrie (Seeligman, Tieke) 1539

Rubber: Manuel pratique de la fabrication du caoutchouc et du produits qui en dérivent (Heil, Esch), 249; Analyse du caoutchouc et de la guttapercha (Pontio), 252; Le caoutchouc (Fayol), 428; The Chemistry of India Rubber (Weber), 896, India Rubber and Gutta-Percha (McIntosh), 1009; Etude sur la production dû caoutchouc dans les colonies Françaises (Chartier), 1110; Le caoutchouc (Tillier).... 1540

Fats, Fatty Oils and Soaps: Die kaustische und kohlensaure Verseifung in der modernen Seifenindustrie. Die Haushaltungsseife (Kirchner), 813; Die Fette und Oele, Darstellung der Gewinnung und der Eigenschaften aller Fette, Oele u. Wachsarten, der Fett u Oelraffinerie u. der Kerzenfabrikation (Thalmann), 896; Einheitsmethoden zur Untersuchung von Fetten, Oelen, Seifen und Glycerinen sowie sonstigen materialien der Seifenindustrie, 1363, Technologie der Fette und Oele (Hefter), 1364; Beitrage zur Chemie u. Analyse der Fette (Heiduschka, Pfizenmaier).... 1537

Sugar: Manuel de la fabrication du sucre de betterave a l'usage des praticiens (Vrancken, Aulard, 253; The Manufacture of Cane Sugar (Jones, School), 429; Beet-Sugar Making and Its Chemical Control (Nikaido), 576; Der Zuckerrübenbau und die Fabrikation des Rübenzuckers, nach den neuesten Erfahrungen der Wissenschaft und der Praxis (Stift, Gredinger), 896; Technical Calculations for Sugar Works (Mittelstaedt), 1111; Ueber massanalytische Methoden zur Bestimmung der Zuckerarten (Lehmann), 1538, Jahresbericht über die Untersuchungen und Fortschritte auf dem Gesamtgebiete der Zuckerfabrikation, 1699; Ueber das Vorkommen von Raffinose in Rohzucker und deren Bestimmung (Strohmer) .. 1699

Leather: The Manufacture of Leather (Bennett), 247, Zur Kenntnis des Gerbprozesses (Schroeder), 576; Lederfabrikation (Krönlein), 813; Die pflanzlichen Gerbstoffe Uebersicht über Vorkommen, Eigenschaften, Gewinnung und Anwendung der wichtigeren pflanzlichen Gerbstoffe (Franke), 895; Practical Tanning (Fleming), 1111; Chemie der Gerbstoffe (Nierenstein).. 1538

Miscellaneous Technology Massendestillation von Wasser (Bothas), 248; Holzverkohlung und der Köhlereibetrieb (Denz), 248; Der Graphit (Haenig), 249, Der Schmirgel und seine Industrie (Haenig), 249; Die Kitte und Klebemittel (Lehner), 250; Calciumcarbid-Fabrikation (Liebetanz), 250, Ueber die Verpuffungs- und Verbrennungsprodukte von Celluloid (Pfyl, Rasenack), 252; Der Oelfarben-Kopierprozess nach Rawlins (Puyo), 252; Die Praxis des Gummidruckverfahrens (Quedenfeldt), 252; Monographien über angewandte Elektrochemie XXXI B Electrolytlytische Zahler (Worden), 254; Die Destillation industrielles und forstwirtschaftlicher Holzabfälle (Harper), 428, The Transportation of Gases, Liquids and Solids, by Means of Steam, Compressed Air and Pressure Water (Nagel), 429; Die Holzstoff und Holzschliff-Fabrikation (Schubert), 430; Grundzüge der Elektrotechnik zum Gebrauche an gewerblichen Lehranstalten (Wolf), 430; Baking Powder and Other Leavening Agents (Foot), 575; Hilfsbuch für den Apparatebau (Hausbrand), 576; Modern Bleaching Agents and Detergents (Bottler), 727; Industrial Diseases and Accidents (Greer), 727; Technologie der Holzverkohlung (Klar), 727; A Practical Manual on Sea Water Distillation (Normandy), 728; Die Entwicklung der Elektrochemie in gemeinverständlicher Darstellung (Ostwald), 728; Die Fabrikation der Glühkörper für Gasglühlicht (Böhm), 813; Chemie für Techniker (Hahn), 813; Einrichtung eines Fabriklaboratoriums (Scheffler), 814; Wood Preservation in the United States (Sherfesee), 814; Les matières abrasives industrielles. Les métaux spéciaux manganèse, chrome, etc. (Escard), 895; Handbuch der Kaliwerke, Salinen, Tiefbohrunternehmungen und Petroleum Industrie (Myer), 895; Le pain, fabrication rationelle historique (Sérand), 896; Die elektrochemischen Patentschriften der Vereinigten Staaten. Bd. I: Elektrothermische Verfahren und Apparate; Entladungen durch Gase (Ferchland), 1008; Handbuch der Kaliwerke, Salinen, Tiefbohrunternehmungen und Petroleum-Industrie, 1009; Jahresbericht über die Leistungen der Chemischen Technologie, mit besonderer Berücksichtigung der Elektrochemie und Gewerbestatistik für das Jahr 1910, 1009; Lehrbuch der technischen Physik (Lorenz), 1009; Das Trocknen u. die Trockner (Marr), 1009; Herstellung und Verwendung der verdichteten und verflüssigten Gase (Schall), 1010; Der Kesselstein, seine Entstehung und Verhütung (Andrés), 1101; Einführung in die technische

Elektrochemie (Askenasy), 1110; Chemisch-technische Spezialitäten und Geheimnisse mit Angabe ihrer Zusammensetzung nach den bewährtesten Chemikern (Capaun-Karlowas), 1110; Chemische Technologie der Neuzeit, 1110; Handbuch der Brikettbereitung (Franke), 1111; Handbuch der deutschen Aktien-Gesellschaften, 1111; The Fire-Resistive Properties of Various Building Materials (Humphrey), 1111; Praktisches Handbuch des Zeugdrucks (Lauber), 1111; Hilfsbuch für Wärme und Kalteschutz (Andersen), 1362; Die mechanische Kälteerzeugung (Ewing), 1363; Jahrbuch der deutschen Braunkohlen-, Steinkohlen- und Kali-Industrie, 1364; Jahrbuch der technischen Sondergebiete, 1364; Lueger's Lexicon gesamten Technik, 1364; Beiträge zur Theorie des Huntington-Heberlein-Prozesses (Richter), 1365; Der elektrische Ofen (Bronn), 1537; Praktische Anleitung zur Inbetriebsetzung Hoffmannscher Ringofen (Burghardt), 1537; Chemische Technologie der Neuzeit (Dammer), 1537; Einrichtung von Fabriklaboratorien (Scheffler), 1539; Le celluloid, fabrication, applications, substituts (Masselon, Cillard), 1699; Allgemeine chemische Technologie (Rauter), 1699; Engineering Chemistry (Stillman), 1699; Handbuch der Fabrikation (Zerr, Rubenkamp).... 1700

NEWELL, L. C. A Course in Inorganic Chemistry for Colleges (book), review 725, title.... 251

NEWTH, G. S. A Text-Book of Inorganic Chemistry (book), 429; Chemical Lecture Experiments (book).... 429

New York section.... Pr. 46, 60, 67, 81, 87, 94, 123

Nickel, electrolytic determination of, 1629; new volumetric method for.... 757

NICOLAS, E. See Porcher, C

NIERENSTEIN, M. Chemie der Gerbstoffe (book).... 1538

NIEWENGLOWSKI, G. H. Traité pratique de photographie des couleurs (book).... 895

NIKAIDO, Y. Beet-Sugar Making and its Chemical Control (book).... 576

Nitrates, determination of, in water, 630; effect of, on the precipitation of barium sulphate.... 613

Nitric acid, silver nitrate formed by the action of, on silver sulphide, 1030, solubility of gold in.. 318

3-Nitro-4-acetaminobenzonitrile, preparation.... 1497

2-*m*-Nitrobenzalacetylnaphthol-1 and properties.... 1484

p-Nitrobenzonitrile, preparation.... 1495

Nitrogen, ammoniacal, application of the Folin method to the determination of, in meat, 561; atomic weight of, 1, 255, 257; determination of ammonia nitrogen in water in the presence of hydrogen sulphide, 1256; estimation of small quantities of nitrogen by Pelouze's reaction, 1237; nitric, influence of chlorine upon the determination of.... 756

Nitroisocampholactone.... 1666, 1668

2-(6-Nitro-3,4-methylenedioxyphenyl)naphthoflavanone and bromine derivative.... 1488

Nitrophenols, preparation of *o*- and *p*-.... 1105

3-Nitrophthalic acid, derivatives of.... 1327

4-Nitrophthalic acid, derivatives of.... 1328

4-Nitrophthalodianilide.... 1322, 1329

3-Nitrophthalo-β-naphthylamidic acid.... 1328

4-Nitrophthalo-β-naphthylamidic acid, 1322; preparation.... 1329

3-Nitrophthalophenylamidic acid, transformation of.... 1327

2-(6-Nitropiperonylalcohol) acetylnaphthol-1.... 1485

1,3,4-Nitrotoluidine, condensation of, with chloral-aniline.... 975

NOBLE, R. P. Extraction apparatus (note).... 1533

NOELTING, F. A. M. Contributions à la connaissance des oxyaldéhydes orthovanillin at l' aldehyde orthovératrique (book).... 429

NORMAN, G. M. Systematic Practical Organic Chemistry (book).... 728

NORMANDY, F. A Practical Manual on Sea Water Distillation (book).... 728

NORTH, H. B. The action of thionyl and sulphuryl chlorides on mercury and mercuric oxide.. 184

North Carolina section.... Pr. 56, 111

Northeastern section.... Pr. 6, 59, 67, 86, 127

NOYES, A. A. Quantitative application of the theory of indicators to volumetric analysis.... 815

NOYES, A. A. and FALK, K. G. The properties of salt solutions in relation to the ionic theory.. 1011

NOYES, A. A., KATO, Y. and SOSMAN, R. B. The hydrolysis of ammonium acetate and the ionization of water at high temperatures.... 159

NOYES, A. A. and STEWART, M. A. The ionization relations of sulphuric acid.... 1133

NOYES, W. A. Molecular rearrangements in the camphor series (V) Mechanism of the reactions by which laurolene is formed, 1068; Report of the Editor of the Journal of the Chemical Society and Chemical Abstracts.... Pr. 15

NOYES, W. A. and DERICK, C. G. Molecular rearrangements in the camphor series (III). Oxidation products of *l*- and *d*-laurolene.... 1061

NOYES, W. A. and HOMBERGER, A. W. Molecular rearrangements in the camphor series, VI. Isocampholactone.... 1665

Noyes, W. A. and Knight, L. Molecular rearrangements in the camphor series, VII. Derivatives of isocamphoric acid; *l*-dihydrohydroxycampholytic acid 1669

Noyes, W. A. and Kyriakides, L. P. Molecular rearrangements in the camphor series (IV). Synthesis of laurolene, 1064; synthesis of the α,α'-dimethyladipic acids, and separation of the racemic acid into optical isomers 1057

Nucleic acids, biochemistry of, 231; analysis of, 234; components of, 235; constitution of, 237

Nutrition, The Elements of the Science of Nutrition (Lusk, book) 1007

Oates, W. M. See Wheeler, A. S.

Obermiller, J. Die orientierenden Einflüsse und der Benzolkern (book) 251

Obituary, Barker, Pr. 113; Cannizzaro, Pr. 97; Dudley, Pr 48, Gibbs, Pr. 69; Goessmann, Pr. 131

Occhialini, A. See Battelli, A.

Occlusion of sulphates by barium sulphate, 592, 608; of sulphuric acid by barium sulphate 603

Octaethyl-3,3′,6,6′ tetramino-9,9′-dihydroxyparadixanthylbenzene-2,4,5,6-tetracarboxylic acid 204

Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxy-*m*-dixanthylbenzene-2,4,5,6-tetracarboxylic acid and derivatives 200, 201, 202

Octamethyl-3,3′,6,6′-tetramino-9,9′-dihydroxy-*p*-dixanthylbenzene-2,3,5,6-tetracarboxylic acid and salts, 202, 203; tetrahydrochloride, 203; ethyl ester dichloride 204

Octamethyl-3,3′,6,6′-tetramino-*m*-dixanthylbenzene-2,4,5,6-tetracarboxylic acid, ethyl ester dichloride, dihydrochloride of 202

Octamethyl-3,3′,6,6′-tetramino-*p*-dixanthylbenzene-2,4,5,6-tetracarboxylic ethyl ester dichloride, dihydrochloride of 204

Octanes, heats of combustion of the 268, 289

Oesterle, O. A. Grundriss der Pharmakochemie (book) 251

Oettingen, A. Die Schule der Physik, besonders für das Selbstudium verfasst (book) 1010

Ohlmüller, W. and Spitta, O. Die Untersuchung und Beurteilung des Wassers und des Abwassers (book) 1365

Oil, of pumpkin seed, 347; of watermelon seed 361

Oleins, hydrocarbons of the wool grease oleins 1071

Oltamus, F. See Karsten, J.

Oppenheimer, C. Die Fermente und ihre Wirkungen (book), 251, Grundriss der anorgan. Chemie (book), 1365; Handuch der Biochemie der Menschen und der Tiere (book) 728

Optical activity, a relation between the chemical constitution and the optical rotatory power of the sugar lactones 338

Optical rotation of crude jalap resin 85

Ores, analysis of, for copper 1277

Organic chemistry. See Chemistry

Organic compounds, action of magnesium upon the vapors of, 388, cause of color in, 795; nitrogenous, in peat soils 396

Organic matter, determination of total sulphur in 977

Organism, fate of the amino acids in the 671

Orloff, J E. Formaldehyd (book) 251

Orthey, M Die Metallhüttenchemie (book) 576

Osborn, T B The Vegetable Protein (book) 251

Oscroft, P. W and Shea, R P. A Manual of Elementary Practical Chemistry (book) 1539

Ostwald, Luther. Hand- und Hilfsbuch zur Ausfuhrung physico-chemischer Messungen (book) 895

Ostwald, W. Die Energie Wissen und Können (book), 251; Die Entwicklung der Elektrochemie in gemeinverständlicher Darstellung (book), 728; Die Forderung des Tages (book), 1539; Die Schule der Chemie (book), 1010, Einführung in die Chemie Ein Lehrbuch für höhere Lehranstalten und zum Selbstunterricht (book), review 722, title 251; Grundriss der Kolloidchemie (book) 251; Kolloidchemische Beihefte (book) review, 245, L' évolution de la chimie (book), 895; The Fundamental Principles of Chemistry (book), review 572, title 251; Ueber Katalyse (book), 1365; see Clarke, F. W.; see Couturat, L.

Ostwald, W. and Morse, H. W. Elementary Modern Chemistry (book), review 574, title 251

Ottersbach, G. Buchheisters Vorschriftenbruch für Drogisten (book) 1539

Otto, C. Eisenreduktion in Puddelofen (book) 251

Ouvrard, L. Industrie du chrome, du manganèse, du nickel et du cobalt (book) 895

Oxalates, of hydrazine 579

Oxalylanthranilic compounds and quinazolines derived therefrom 119

Oxalyldianthranil 122

Oxalyldianthranilic acid 121

Oxanilido-di-o-carboxylic acid 124

Oxidation of β-naphthoquinone 117

Oxidation products of *l*- and *d*-laurolene ... 1061
Oxygen, basic properties of, 542, 1330; ratio of, to lithium chloride ... 35

Paczkowski. Schädliche Nebenwirkungen der Arzneimittel (book) ... 429
Paech. See Wentzel.
Paine, H. S. See Hudson, C. S.
Palladium, atomic weight of ... 3, 265
Pancreatin, experiments on ... 1080
Paraffinic acid, $C_{24}H_{48}O_2$ ... 1677
Parma, A. Ueber ökonomischen Kohlenverbrauch (book) ... 1539
Parsons, C. L. Chemistry and Literature of Beryllium (book), 251; see Moses, A. J.
Parsons, C. L. and Corliss, H. P. Equilibrium in the system, potassium iodide, iodine and aqueous alcohol ... 1367
Parsons, C. L. and Corson, H. P. The solubility of barium nitrate and barium hydroxide in the presence of each other ... 1383
Parsons, C. L. and Evans, W. W. Diffusion phenomena of the alums ... 1378
Parsons, C. L. and Perkins, C. L. The solubility of strontium nitrate and strontium hydroxide in the presence of each other ... 1387
Partheil, A. Lehrbuch der Chemie (book) ... 252
Partridge, W. See Moor, C. G.
Passive state, influence of the magnetic field on the, of iron ... 750
Passon, M. Kleines Handwörterbuch der Agrikulturchemie (book) ... 728, 895
Peat, analysis of weathered brown ... 407
Peat soils, organic nitrogenous compounds in ... 396
Pécheux, H. Précis de métallurgie (book) ... 1539
Pechmann, H. Anleitung zur quantitativen chemischen Gewichtsanalyse nach C. Zimmermann (book) ... 1010
Peckham, S. F. Solid Bitumens (book) ... 576
Peirce, G. The deviation of ferment action from the monomolecular law with especial reference to the esterases ... 1517
Pelet-Jolivet, L. Die Theorie des Färbeprozesses (book) ... 1010
Pelouze's reaction, estimation of small quantities of nitrogen by ... 1237
Pennington, M. E. and Greenlee, A. D. An application of the Folin method to the determination of the ammoniacal nitrogen in meat ... 561
Pennington, M. E. and Hepburn, J. S. The determination of the acid value of crude fat and its application in the detection of aged foods ... 568
Pentosans in soils ... 1680
Perchloric acid, preparation of, from sodium perchlorate ... 66
Percival. Agricultural Bacteriology, Theoretical and Practical (book) ... 1539
Perkin, F. M. Choix de prèparations de chemie inorganique (book), 1010; Qualitative Chemical Analysis, Organic and Inorganic (book) ... 1365
Perkin, W. H. See Kipping, F. S.
Perkin, W. H. and Lean, B. An Introduction to Chemistry and Physics (book) ... 429
Perkins, C. L. See Parsons, C. L.
Perrin, J. Die Brownsche Bewegung u. die wahre Existenz de Moleküle (book) ... 1365
Peters, H. Aus pharmazeutischer Vorzeit (book) ... 1365
Peyre, R. La céramique française (book) ... 1539
Pfizenmaier, K. See Heiduschka, A.
Pfyl, B. and Rasenack, P. Ueber die Verpuffungs- und Verbrennungsprodukte von Celluloid (book) ... 252
Phenolsulphonic acid, method for determination of nitrates in water ... 630
Phenylcamphoformenaminecarboxylic acid, preparation and reactions, 1505; dibenzylamine salt, 1504, 1514; methyl ester, 1500, ... 1507
Phenyl ether and some of its derivatives ... 1285
Phenylethylammonium methylsulphate ... 766
1-Phenyl-2-methoxymethylthiourea ... 1284
1-Phenyl-2,2-methyl-*p*-nitrophenylethylthiourea ... 768
3-Phenyl-4-phenyliminoquinazoline-2-carboxylic acid, ethyl ester ... 125
Phenylpropiolic series, acids of, and their condensation to naphthalene derivatives ... 212
3-Phenyl-4-quinazolone-2-carboxylic acid methyl and ethyl esters ... 125
Philadelphia section ... Pr. 4, 58, 68, 92, 111, 127
Philip, J. C. Physical Chemistry; its Bearing on Biology and Medicine (book), 1539; The Romance of Modern Chemistry (book) ... 252
Phosphates of calcium ... 869

Phosphoric acid, rate of hydration of pyrophosphoric acid 1576
Phosphorus, atomic weight 2, 259, 298, 1114
Phthalic acid, action of amines on 113, 1319
Phthalocamphylimide 115
Piccard, J. F. Ueber Konstitution und Farbe der Chinonimine (book) 728
Pick and Conrad. Die Herstellung von hochprozentigen Ferrosilicium im elektrischen Ofen (book) 252
Pirk, E. Die Oelfeuerung im Schmiedebetrieb und in der Metallwarenfabrikation (book) 1365
Pierron, L. See Desalme, J.
Piest, C. Die Cellulose (book) 1539
Piperonylidene-*m*-aminodimethylaniline 386
Piperonyloin, some properties of, 1492; ureide, 1493; thioureide 1494
Pittsburg section .... Pr. 44, 57, 85, 126
Plant food, rate of extraction of, from the phosphates of calcium and from a loam soil 879
Platinum, atomic weight of 266, 1115
Platinum black, preparation of (note) 336
Plato, F. Tafel zur Umrechnung der Volumprozente in Gewichtsprozente und der Gewichtsprozente in Volumprozente bei Branntweinen. Berechnet nach den amtlichen Zahlen der Kaiserlichen Normal-Eichungskomission (book) 576
Plotnikov. Photochemie (book) 814
Pöschl, V Die Härte der festen Körper und ihre physikalisch-chemische Bedeutung (book), 252; Einführung in die Kolloidchemie (book) 814
Polyiodides, equilibrium between iodine, iodide and, in aqueous solution 914
Pontio, M. Analyse du caoutchouc et de la guttapercha (book) 252
Porcher, C. et Nicolas, E. Cours de chimie organique at biologique (book) 1010
Potash bulb 1691
Potassium, in sea water, 647; speedy detection of, in small amounts 78
Potassium aluminium alum, diffusion of 1380
Potassium chrome alum, diffusion of 1380, 1382
Potassium dichromate, reaction between ammonium chloride and, when heated 178
Potassium iodide, conductance and ionization of the triiodide, 914; equilibrium in the system: iodine, aqueous alcohol and, 1367; equivalent conductance of 919
Potassium permanganate, a source of error in titration with 1204
Potential, of iron calculated from equilibria measurements, 1214, of the sodium electrode, 1459, 1466; of the thallium electrode, 732, the Marsh test and excess 518
Poulsen, A. Cement in Sea Water (book) 576; Zement m Meerwasser (book) 814
Poulsson, E. Lehrbuch der Pharmakologie (book) 252
Power, F. B and Rogerson, H Chemical examination of jalap 80
Power, F. B. and Salway, A. H Chemical examination of pumpkin seed, 346; chemical examination of water-melon seed 306
Pozzi-Escot, E. Les synthèses dans le groupe de l' indigo (book) 895
Prag, E. A Course in Dyeing for Garment Dyers (book) 728
Pratt, D. S. See Chamot, E. M.
Pratt, L. A. See James, C.
Precipitation of the iron group 953
Preparations, Anleitung für das organisch präparative Praktikum (Henle, book) 245
Prescher, and Rabs Bakteriologisch-chemisches Praktikum (book) 1699
Preservation of feces 1683
7-Propionamino-2-methyl-4-quinazolone 1304
Proteins, determination of iodine in protein combinations 692
Proumen, H. J. La matière, l'éther, l'électricité (book) 1539
Pseudoammonium bases, ether-thioureas and their relation to, 1279; and their alcoholates 1279
Pseudolaurolene 1068
Publow, C. A. and Troy, H. C Questions and Answers on Milk Testing (book) 895
Puget Sound section .... Pr. 56, 65, 96
Pumpkin seed, chemical examination of 346
Puyo, C. Der Oelfarben-Kopierprozess nach Rawlins (book) 252

Quedenfeldt, E. Die Praxis des Gummidruckverfahrens (book) 252
Quinazolines, researches on, 119, 1297, 1654; review 784
4-Quinazolone-2-carboxylic acid and ammonium salt and ethyl ester 122
4-Quinazolone group, the synthesis of some stilbazoles, hydrazones and Schiff bases in the 1654
Quinazolones from 4-acetaminoacetanthranil, 1301; ; from 5-acetaminoacetoanthranil 1311

Rabow, S. Arzneiverordnungen 1910. Die neuesten Arzneimittel und Spezialitäten (book). 1111
Rabs. See Prescher.
Racemic form of α,α'-dimethyladipic acid, separation into optical isomers 1057, 1060
Rack for holding reagents in bulk... 884
Radford, W. A. Cement and How to Use it (book) ... 1111
Radiochemistry (Cameron, book) ... 1106
Radium, atomic weight of, 267; Das Radium und die Farben (Dölter, book) ... 724
Rafsky, H. R. See Torrey, H. A.
Ragno, S. La soudure autogène des métaux (book) ... 895
Rakusin, M A. Die Theorie der Färbung der natürlichen Erdöle und deren notwendige Konsequenzen (book) ... 252
Randall, D. L. The reaction between hydriodic acid and bromic acid in the presence of a large amount of hydrochloric acid ... 644
Rasenack, P. See Pfyl, B.
Rauter, G. Allgemeine chemische Technologie (book) ... 1699
Reaction, a study of the reaction, $KHg_m + Na^{\cdot} \rightleftarrows K^{\cdot} + NaHg_n + (m\text{-}n)Hg$, 502; is the hydrolysis of cane sugar by acids a unimolecular, when observed with a polariscope? 885; rearrangements with, 1344; metathetical reactions ... 1279
Reagent bottle, new normal solution and ... 1277
Rearrangements, classes of, 1346; with reaction, 1344; in the camphor series, 1061, 1064, 1068, 1665, 1699; of carbon compounds, 1333; of unsaturated acids ... 1339
Rechenberg, C. v Theorie der Gewinnung und Trennung der ätherischen Oele durch Destillation (book) ... 1539
Reduction of titanifluorides by alkali metals, 331; of titanium dioxide by carbon, 332, of titanium tetrachloride with sodium ... 333
Reid, J. Practical Sanitation (book) ... 1539
Remsen, I. An Introduction to the Study of Compounds of Carbon (book) ... 728
Remsen–Seubert Anorganische Chemie (book), 252; Einleitung in das Studium der Chemie (book) ... 252
Rengade, E. Analyse thermique et métallographie microscopique (book) ... 814, 896
Renker, M Ueber Bestimmungsmethoden der Cellulose (book) ... 1539
Renshaw, R R. Preparation of choline and some of its salts ... 128
Renshaw, R R. and **Atkins**, K. N. Bactericidal properties of lecithins and choline salts ... 130
Renshaw, R R and **Ware**, F. C Studies in the action of heat on milk ... 391
Report of the International Committee on Atomic Weights, 1910 ... 1, 1113
Research, organization of industrial ... 71
Resolutions on the death of Charles Benjamin Dudley ... Pr. 32
Retene, the constitution of, and its derivatives ... 394
Rettberg, H. Abbau des Morphobetains, II. Ueber einige Additionsprodukte cyclischer Basen mit Hydrochinon (book) ... 1539
Rhamnose, stereo-configuration of ... 345
Rhodamines, constitution of, of mellitic acid ... 190
Rhode Island section ... Pr. 6, 58, 66, 81, 86, 93, 112, 123
Rhodeose, partial stereo-configurations of ... 345
Rhodium, atomic weight of ... 264, 1115
Richards, E. H. and **Woodman**, A. G. Air, Water and Food from a Sanitary Standpoint (book) 1365
Richards, R. H. Text-Book of Ore Dressing (book) ... 728
Richards, T. W. Experimentelle Untersuchungen über Atomgewichte (book), review ... 242
Richards, T. W. and **Baxter**, G. P. Concerning the correction of the apparent weight of a salt to the vacuum standard ... 507
Richards, T. W. and **Burgess**, L. L. The adiabatic determination of the heat of solution of metals in acids (I) ... 431
Richards, T. W. and **Hönigschmid**, O. A revision of the atomic weight of calcium I. Analysis of calcium bromide ... 1577
Richards, T. W. and **Jesse**, R. H., Jr. The heats of combustion of the octanes and xylenes... 268
Richards, T. W., **Rowe**, A. W. and **Burgess**, L. L. The adiabatic determination of heats of solution of metals in acids (II) ... 1176
Richards, T. W. and **Willard**, H. H. Further investigation concerning the atomic weights of silver, lithium and chlorine ... 4
Richards, T., **Wilson**, J. H. and **Garrod-Thomas**, R. N. Electrochemical Investigation of Liquid Amalgams of Thallium, Indium, Tin, Zinc, Cadmium, Lead, Copper and Lithium (book) ... 111[illegible] 552
Richardson, C. Grahamite, a solid native bitumen ... 2[illegible]
Richardson, W. D. Report of the "Journal of Industrial and Engineering Chemistry" for the year 1909 ... 103[illegible] ... Pr. 17

Richter, K. Zink, Zinn, und Blei (book)........ 252
Richter, M. M. Lexikon der Kohlenstoffverbindungen (book)........ 1539
Richter, P. Beiträge zur Theorie des Huntington-Heberlein-Prozesses (book)........ 1365
Richter, V. v. Lehrbuch der anorganischen Chemie (book)........ 1539
Ricke, R Porzellan (book), 814; Das Porzellan (book)........ 1699
Ries, H. History of the Clay-working Industry in the United States (book)........ 252
Riesenfeld, E H. Anorganisch-chemisches Praktikum Qualitative Analyse und anorganische Prapärate (book)........ 1539
Rievel, H. Handbuch der Milchkunde (book)........ 1539
Riggs, L. W. The determination of iodine in protein combustion (II)........ 692
Righi, A. La materia radiante ed i Raggi magnentici (book)........ 1010
Rimbach, E. Chemisches Praktikum für Mediziner (book)........ 728
Rinne, F. Zur chemisch-mineralogischen Erforschung der Deutschen Kalisalzlagstätten (book)........ 896
Ripening, stimulation of premature, by chemical means........ 208
Rippel, J. Grundlinien der Chemie für Oberrealschulen (book)........ 576
Rivals, P. and Devaud, M. Chemie (book)........ 1539
Robertson, T. B. The Proteins (book)........ 728
Robertson, W G. Manual of Medical Jurisprudence, Toxicology and Health (book)........ 1112
Robinson, C H. Note on the oxidation of β-naphthoquinone........ 117
Rocks, Analyse der Silikat- und Karbonat-Gesteine (Hillebrand, book)........ 724
Rockwood, E W. An Introduction to Chemical Analysis for Students of Medicine, Pharmacy and Dentistry (book), review........ 243
Rodger, N. Wall Charts for Sugar Chemists (book), review........ 811
Roehrich, V. H See Frankforter, G. B
Röttger, H. Lehrbuch der Nahrungsmittel-chemie (book)........ 896, 1010
Rogerson, H See Power, F. B
Rosanow, N Kursus der physiologischen Chemie mit Anleitung zur qualitativen und quantitativen Analyse des Harns (book)........ 1539
Roschke, K. Ueber α Oxolaktame (book)........ 576
Rose, J. D An adjustable automatic burette (note)........ 703
Rossmässler, F A Die flüssigen Heizmaterialien und ihre Anwendung (book)........ 252
Rost, E. F. F and Heise, R. Beiträge zur Photographie der Blutspektra unter Berücksichtigung der Toxikologie der Ameisensäure (book)........ 429
Roth, W. A Exercises in Physical Chemistry (book)........ 252
Rothschild, M Ueber Synthesen ringformiger Verbindungen mittels Dipropylmalonylchlorids und Succinylchlorids (book)........ 728
Rousset, H. See Chaplet, A.
Rousset, H. and Chaplet, A Les combustions industrielles (book)........ 252
Routala, F. O. Ueber die Bildung der Naphthene im Erdöl (book)........ 728
Rowe, A W. See Richards, T. W
Roy, C. S See Silberrad, O
Rubenkamp, R See Zerr, G.
Rudnick, P A modified burette for standard alkali solutions (note)........ 971
Rudolf, W Die Tonwarenerzeugung mit besonderer Berücksichtigung der chemischen Grundlagen (book)........ 1010
Rudolph Keramik (book)........ 430
Rübencamp, R See Zerr, G.
Rüdisüle, A. Die Untersuchungsmethoden des Eisens und Stahls (book)........ 1699
Ruer, R. The Elements of Metallography (book), review 246, title........ 430
Rulon, S. A., Jr, and Hawk, P. B. Studies on water drinking. III. On the uric acid elimination following copious water drinking between meals........ 1686
Rupe, H. Anleitung zum Experimentieren in der Vorlesung über organische Chemie (book), review........ 141
Rupert, F. F. The solid hydrates of ammonia (II)........ 748
Ruska, J. Leitfaden der Mineralogie (book)........ 896
Rutherford, T. A. See Howe, P. E.

Saint-Giles, P. de. See Berthelot.
St. Louis section........ Pr. 46, 65, 79, 87, 97, 126
Salicylic acid in pumpkin seed........ 352
Salts, colored, Schiff's base, 382; concerning the correction of the apparent weight of a salt to

the vacuum standard, 507; double formation of, 618; ionization of, in mixtures with no common ion, 741; of bases formed by condensing *m*-aminodimethylaniline and *m*-aminodiethylaniline with aromatic aldehydes, 382; properties of salt solutions................ 1011
SALWAY, A. H. See Power, F. B.
SANG, A. The Corrosion of Iron and Steel (book)................................ 814
SAVOLA, H. Metallography Applied to Siderurgic Products (book)................ 1010
SCALA, A. See Mengarini.
SCHÄFER, A. Einrichtung und Betrieb eines Gaswerkes (book)..................... 1010
SCHAEFER, F. Die wirtschaftliche Bedeutung der techn. Entwicklung in der Papierfabrikation (book).. 252
SCHÄTZLEIN, C. Zuckerungstabellen zur gesetzlich erlaubten Verbesserung der Traubensäfte, Traubenmaischen und Weine, sowie der Obst- und Beerensäfte (book)............ 430
SCHALL, M. Herstellung und Verwendung der verdichteten und verflüssigten Gase (book).. 1010
SCHALLER, W. See Hillebrand, W. F.
SCHEFFLER, W. Einrichtung von Fabriklaboratoriums (book).................... 814, 1539
SCHEINER, J. Spektralanalytische und photometrische Theorien (book)............ 430
SCHENK, E. Ueber die Reduktion von Pinen zu Pinan; Eigenschaften und chem. Verhalten des letzteren (book).. 1540
Schiff bases, the synthesis of some, in the 4-quinazolone group................ 1654
SCHIFFERERS Praktische Malzerei- und Brauerei-Betriebskontrolle (book)........ 1010
SCHIPPMAN, W. Aus der Praxis eines Glashüttenfachmannes (book)................ 814
SCHLOSSMANN, A. Leitfaden der Milchhygiene (book)............................ 814
SCHLUNT, H. and MOORE, R. B. Radioactivity of the Thermal waters of Yellowstone National Park (book).. 1365
SCHMIDT, H. Die photographische Praxis (book)................................ 252
SCHMIDT, J. Der Aether und seine Aggregatzustande (book), 814; Jahrbuch der organischen Chemie (book).. 1010
SCHMIDT, M. R. A colorimetric determination of manganese in the presence of iron.......... 965
SCHMIDT, W. Atomauflösung u elektromotorische Kraft (book).................... 1365
SCHMIDT, W A. Die Erkennung von Blutflecken und die Unterscheidung von Menschen- und Tierblut in der Gerichtspraxis, zugleich eine Schilderung der Haupteigenschaften des Blutes, sowie der Blutverwandtschaft unter den Tieren (book)................ 430
SCHMIEDERBERG, O. Grundriss der Pharmakologie in Bezug auf Arzeneimittellehre und Toxikologie (book).. 252
SCHNEIDER, W. Mineralische Düngemittel u. Ernteergebnisse (book)................ 430
SCHNEIDEWIND, W. Die Kalidüngung (book)...................................... 1365
SCHOLTZ, M. Lehrbuch der pharmazeutischen Chemie (book)...................... 1539
SCHOOL, F. J. See Jones, L.
SCHOORL, N. Beiträge zur mikrochemischen Analyse (book)...................... 252
SCHREIBER, H. The determination of total sulphur in organic matter............ 977
SCHREINER, O. and SHOREY, E. C. Some acid constituents of soil humus........... 1674
SCHROEDER, J. v Zur Kenntnis des Gerbprozesses (book)......................... 576
SCHUBERT, M. Die Holzstoff und Holzschliff-Fabrikation (book).................. 430
SCHÜTZ, E. Hüttenmännische Probierkunde (book)................................ 1010
SCHUMANN, A. Wie scheidet man Nickel am besten ab auf elektrolyt. Weg? (book).......... 252
SCHUMM, O. Klinische Spektroskopie (book)...................................... 430
SCHWALBE, C. G. Die Chemie der Cellulose, unter besonderer Berücksichtigung der Textil- u. Zellstoffindustrien (book).. 1699
SCHWENZER, P. See Kraus, A.
Science, An Introduction to Physical Science (Getman, book).................... 142
SEAMAN, W. H. A Manual for Assayers and Chemists (book)........................ 1699
Sea water. See Water.
SEELIGMANN, F. and TIEKE, E. Handbuch der Lach- und Firnis-Industrie (book).......... 1539
SEGERBLOM, W. First Year Chemistry (book), review............................. 139
SELLERS, J. F. Treatise on Qualitative Analysis (book), review 242, title....... 430
SÉRAND. Le pain, fabrication rationelle historique (book)...................... 896
SEUBERT, K. Internationale Atomgewichte. Nach den Festsetzungen des internationalen Atomgewichts Ausschusses herausgegeben (book)................................ 253
SEXTON, A. H. Fuel and Refractory Materials (book)............................ 728
SHARP, J. Modern Foundry Practice (book)...................................... 1365
SHEA, R. P. See Oscroft, P. W.
SHERFESEE, W. F. Wood Preservation in the United States (book)................ 814
SHERMAN, H. and HIGGINS, H. L. The composition of some Benzali food materials.......... 558
SHERMAN, H. C. See Kendall, E. C.

Sherman, H. C., Kendall, E. C. and Clark, E. D. Studies on amylases (I). An examination of diastatic power.... 1073

Sherrill, M. S. The ionization of salts in mixtures with no common ion.... 741

Shorey, E. C. See Schreiner, O.

Shorey, E. C. and Lathrop, E. C. Pentosans in soils.... 1680

Sidersky, D. La réfractométrie et ses applications pratiques (book).... 576, 1699

Silberberg, L. Gesetz über Absatz von Kalisalzen vorm 23 Mai 1910 (book).... 1699

Silberrad, O. and Roy, C. S. The condensation products of mellitic acid with metaaminophenol and their bearing on the relationship of color and fluorescence to constitution.... 189

Silicates, Analyse der Silikat- und Karbonat-Gesteine (Hillebrand, book).... 724

Silver, atomic weight, 2, 4, 257, 1591, character of silver deposits from various electrolytes, 1571; determination of the silver corresponding to calcium bromide, 1586; rapid determination of, by means of the mercury cathode and stationary anode, 1231; ratio of lithium chloride to.... 31

Silver bromide, determination of the relation of calcium bromide to.... 1588

Silver chloride, conductance of saturated solutions, 53; precipitation and weighing of, 28; ratio of lithium chloride to, 4, solubility of, at high temperatures.... 50

Silver nitrate, formed by the action of nitric acid on silver sulphide.... 1030

Silver phosphate, analysis of, 298, preparation of, 303, specific gravity of.... 314

Silver sulphide, silver nitrate formed by the action of nitric acid on.... 1030

Simmersbach, F. Die geologischen Unterlagen des Radiums (book).... 1010

Simon, O. Laboratoriumsbuch für die Industrie der Riechstoffe (book).... 728

Siphon, an improved.... 810

Sloan, W. H. On the preparation of a cuprous nitrate, $CuNO_3.2NH_3$ (note), 972; the conductivity of some concentrated aqueous solutions at zero.... 946

Smiles, S. The Relations between Chemical Constitution and Some Physical Properties (book) 1539

Smith, A. Does calomel furnish another contradiction of the theory of heterogeneous dissociation equilibrium?, 187; Einführung in die allgemeine und anorganische Chemie auf elementare Grundläge (book), review 426, General Chemistry for Colleges (book), review. 427

Smith, A. and Menzies, A. W. C. A common thermometric error in the determination of boiling points under reduced pressure, 905; studies in vapor pressure: (I) A method for determining under constant conditions the boiling points of even minute quantities of liquids and of non-fusing solids, 897; (II) A simple dynamic method applicable to both solids and liquids, for determining vapor pressures and also boiling points at standard pressures, 907; (III) A static method for determining the vapor pressure of solids and liquids, 1412; (IV) A redetermination of the vapor pressures of mercury from 250° to 435°, 1434; (V) A dynamic method for measuring vapor pressures with its application to benzene and ammonium chloride, 1448; (VI) A quantitative study of the constitution of calomel vapor.... 1541

Smith, E. F. George Frederic Barker (obituary), Pr. 113, see Buckminster, I. H.; see Goldbaum, J. S.; see Kollock, L. G.

Smith, G. McP. Heterogeneous equilibria between aqueous and metallic solutions: the interaction of mixed salt solutions and liquid amalgams (I).... 502

Smith, G. McP. and Bennett, H. C. Additional notes on the alkali and alkali earth amalgams 622

Smith, J. C. Oxide of Zinc, its Nature, Properties and Uses (book).... 253

Smith, J. R. Modern Assaying (book).... 1365

Sodium, heat of solution of, in mercury, 1466; in sea water.... 647

Sodium acetate, equivalent conductance of.... 161

Sodium amalgam, electrode potential of dilute.... 1460

Sodium electrode, the potential of the.... 1459, 1466

Sodium hydrogen sulphate, solutions of.... 1151

Sodium perchlorate, preparation of perchloric acid from.... 66

Soils, organic nitrogenous compounds in peat soils, 396; pentosans in, 1680; rate of extraction of plant food constituents from a loam soil, 879; some acid constituents of soil humus.... 1674

Solids, determining under constant conditions the boiling points of non-fusing, 897; determining vapor pressures and boiling points of, at standard pressures, 907; static method for determining the vapor pressures of.... 1412

Solubility of barium nitrate and barium hydroxide in the presence of each other, 1383; of calomel vapor in mercury, 1551; of gold in nitric acid, 318; of silver chloride, barium sulphate and calcium sulphate at high temperatures, 50; of strontium nitrate and strontium hydroxide in the presence of each other.... 1387

Solubility product, the inconstancy of the.... 1186

Solutions, colligative properties of, 496; conductivity of some concentrated aqueous, at zero, 946; heat of dilution of acid, 1176; heterogeneous equilibria between aqueous and metallic, the

interaction of mixed salt solutions and liquid amalgams, 502; new bottle for normal solutions, 1277; properties of salt solutions in relation to the ionic theory, 1011; the fundamental law for a general theory of 653, 1636
Sommer, E. Ueber die Radioaktivitätsverhältnisse der natürlichen Heilquellen des Deutschen Sprachgebietes (book) 1539
Sommerfeld, P. Milch und Molkereiprodukte; ihre Eigenschaften, Zusammensetzung und Gewinnung (book) 896
Soncini, T. L'ambiente chimico ed i fermenti selezionati (book) 896
Sosman, R. B. See Noyes, A. A.
Spear, E. B. The causes of the high results in the electrolytic determination of zinc 533
Spear, E. B., Wells, E. E. and Dyer, B. Electrolytic determination of zinc 530
Specific gravity. See Density.
Sperber, J. Leitfaden für den Unterricht in der anorganischen Chemie didaktisch bearbeitet (book) review 1534, title 253
Speter, M. Lavoisier und seine Vorläufer (book) 1112
Spiegel, L. Chemische Konstitution und physiologische Wirkung (book) 253
Spilker, A. Kokerei und Teerprodukte der Steinkohle (book) 253
Spitta, O. See Ohlmüller, W.
Sporer, J. L. Rack for holding reagents in bulk (note) 884
Stähler, A. See Stock, A.
Standardization, resolutions governing committees of the American Chemical Society, and of its divisions, having to do with the, of methods of analysis .... Pr. 106
Stange, A. Illustr. Jahrbuch der Wirtschaft und Technik im deutschen Kalisalzbergbau, nebst Reichskaligesetz mit einer krit. Einleitung (book) 1699
Steensma, F. A. Methoden der chemische en microscopische Diagnostiek (book) 1539
Steinhorst, H. Studien über Konstitutionsermittelung monohalogenisierter, mono- und dialkylierter Monoketone der Cyclohexanreihe (book) 1366
Step, J. Das Radium und seine Eigenschaften (book) 253
Stereochemistry 425
Stevenson, R. See Baskerville, C.
Stewart, A. W. Recent Advances in Physical and Inorganic Chemistry (book), review 574, title 253
Stewart, M. A. See Noyes, A. A.
Stewart, R. and Greaves, J. E. The influence of chlorine upon the determination of nitric nitrogen 756
Steyer, G. See Fess, F.
Stieglitz, J. Catalysis on the basis of work with imido esters 221
Stift, A. und Gredinger, W. Der Zuckerrübenbau und die Fabrikation des Rübenzuckers, nach den neuesten Erfahrungen der Wissenschaft und der Praxis (book) 896
Stilbazoles, the synthesis of some 1654
Stillman, T. Engineering Chemistry (book) 1699
Stock, A. and Stähler, A. Praktikum der quantitativen anorganischen Analyse (book) 430
Strohmer, F. Ueber das Vorkommen von Raffinose in Rohzucker und deren Bestimmung (book) 1699
Strontium, atomic weight, 1114; metallic 1222
Strontium hydroxide, solubility of strontium nitrate and in the presence of each other 1387
Strontium nitrate, solubility of strontium hydroxide and in the presence of each other 1387
Strzyzowski, C. Cours de chemie physiologique et pathologique (book) 1540
Stutzer, A. Düngerlehre (book) 1366
2-Styryl-7-acetamino-4-quinazolone 1662
2-Styryl-3-amino-4-quinazolone 1660
2-Styryl-3-benzalamino-6-acetamino-4-quinazolone 1664
2-Styryl-3-benzalamino-7-acetamino-4-quinazolone 1664
2-Styryl-3-benzalamino-4-quinazolone, 1659; hydrochloride 1660
2-Styryl 3 benzoylamino-4-quinazolone 1660
2-Styryl-3,7-diacetamino-4-quinazolone 1664
2-Styryl-3,7-dibenzalamino-4-quinazolone 1663
2-Styryl-4-hydroxyquinazoline 1657
2-Styryl-3-methyl-7-acetamino-4-quinazolone 1663
2-Styryl-3-methyl-7-amino-4-quinazolone 1663
2-Styryl-3-methyl-4-quinazolone 1658
2-Styryl-4-quinazolone 1657
2-Styryl-3-salicalamino-4-quinazolone 1661
Sucrose, action of, in preventing destruction of invertase, 1353; inversion of, by invertase, 774, 985, 1220, 1350; is its hydrolysis by acids a unimolecular reaction when observed with a polariscope? 88

SUDBOROUGH, J. J. and CAMPBELL, J. T. Practical Organic Chemistry (book) ... 728
Sugar, heat of combustion of ... 276
Sugar analysis, Wall Charts for Sugar Chemists (Rodgers, book) ... 811
Sugar lactones, relation between the chemical constitution and the optical rotatory power ... 338
Sugars, a review of discoveries on the mutarotation of the, 889; determination of the constitution of ... 343
Sulphates, exact determination of sulphur in soluble, 388, occlusion of, by barium sulphate.. 592, 608
Sulphur, determination of total, in organic matter, 977; exact determination of, in soluble sulphates 588
Sulphuric acid, in sea water, 648; ionization relations of, 1133; occluded by barium sulphate precipitates, 603; volatilization of, when precipitates are heated ... 597
Sulphuryl chloride, action of, on mercury and mercuric oxide ... 184
SUMNER, J. B See Torrey, H. A.
SURFACE, G. T The Story of Sugar (book) ... 253
Surface energy ... 1162
Surface tension ... 1162
SUTHERLAND, G A. A System of Diet and Dietetics (book), review ... 145
SVEDBERG, THE Die Methoden zur Herstellung kolloider Lösungen anorganischen Stoffe (book), review 146, title ... 253
SWETT, O D. Apparatus for the determination of arsenic ... 962
SYLLWASSCHY, E Die Giftprüfung und die Konzession zum Handel mit Giften (book) ... 728
Synthesis of 6- and 7-amino-2-methyl-4-quinazolones from 4- and 5-acetaminoacetanthranils, 1297, of α,α'-dimethyladipic acids, 1057; of dimethylphenylethylamine, 761, of ethyl tannate from ethyl gallate and glucose, 1318, of laurolene, 1064, of some stilbazoles, hydrazones and Schiff bases in the 4-quinazolone group ... 1654
Syracuse section ... Pr. 47, 60, 67, 86, 97, 124

TAKA DIASTASE, experiments on ... 1077
TALBOT, H P Charles Benjamin Dudley (obituary) ... Pr. 48
Tantalum, atomic weight, 1127; halide bases of ... 323
Tantalum bromides ... 323
Tantalum chloride, preparation of, 1129; density of, 1131, analysis of ... 1131
Tantalum halides ... 729
TAPPEINER, H v Lehrbuch der Arzneimittellehre und Arzneiverordnungslehre (book) ... 1366
Tautomerism ... 421
TEICHERT, K Methoden zur Untersuchung von Milch und Molkereiprodukten (book) ... 253
Tellurium, atomic weight of ... 2, 262, 1115
TENNANT, A The American Annual of Photography (book) ... 430
Ternary diagram ... 1408, 1410
Tetrabromophenyl ether ... 1286
Tetrabromo m-tolyl ether ... 1287
Tetrachlorophthalo-β-naphthalo-β-naphthylimide ... 1327
Tetrachlorophthalo-β-naphthylamidic acid, 1320, 1326; sodium and potassium salts ... 1326
Tetrachlorophthalophenylamidic acid and its sodium and potassium salts ... 1320, 1325
Tetrachlorophthalophenylimide, preparation of ... 1325
Tetrachlorophthalo-o-tolylamidic acid ... 1320
Tetraethyl 3,6-diamino-9-hydroxyxanthylbenzenepentacarboxylic acid ... 200
Tetramethyl-3,6-diamino-9-hydroxyxanthylbenzenepentacarboxylic acid, ethyl ester chloride, 199; hydrochloride of same, 200, potassium and silver salts of acid ... 198, 199
Tetramethyl-3,6-diaminotetraethyl-$3',6'$-diamino-$9,9'$-dihydroxymetadixanthylbenzene-2,4,5,6-tetracarboxylic acid ... 205
Thallium, effect of thallous ion concentration upon the potential of ... 733
Thallium, electrode potential of ... 732
Thallium sulphate, transference data for thallous sulphate, 1561; transference experiments with lead nitrate and thallous sulphate ... 1555
THALMANN, F. Die Fette und Oele, Darstellung der Gewinnung und der Eigenschaften aller Fette, Oele u Wachsarten, der Fett u. Oelraffinerie u. der Kerzenfabrikation (book) ... 896
Thermodynamic chemistry, a simple system of, based upon a modification of the method of Carnot ... 467, 1636
Thermodynamic engine, the perfect ... 469
Thermodynamic potential system, Gibbs' ... 664
Thionyl chloride, action of, on mercury and mercuric oxide ... 184
Thioquinazolines (review) ... 792
Thiosemicarbazylcamphoformenaminecarboxylactimide ... 1502, 1510

Thiosemicarbazylcamphoformenaminecarboxylic acid and ethyl ester.......1501, 1502, 1509, 1510
THOMAS, P. See Bertrand, G.
THOMAS, V. Guide pratique de teinture moderne, suivi de l'art du teinturier dégraisseur (book) 1540
THOMPSON, C. J. S. The Compendium of Medicine and Pharmacy (book).................... 1366
THOMPSON, S. P. The Life of William Thompson, Baron Kelvin of Largs (book)............ 1112
THOMS, H. Arbeiten aus dem pharmazeutischen Institut der Universität Berlin (book)....... 1540
THOMSON, SIR W. (LORD KELVIN). Mathematical and Physical Papers· Bd. IV. Hydrodynamics and General Dynamics (book).. 1366
THORPE, E. History of Chemistry (book), review 1693, title.............................. 430
THORPE, T. E. See Clarke, F. W.
Thulium.. 517
TIEKE, E. See Seeligmann, F.
TIGERSTEDT, R. Lehrbuch der Physiologie des Menschen (book)....................... 1010
TILDEN, W. A. The Elements (book).. 1699
TILLIER, L. Le caoutchouc (book).. 1540
Tin alloys, analysis of tin-antimony alloys.. 1241
TINGLE, A. The action of coke on solutions of ferric chloride (note)..................... 540
TINGLE, J. B. and BATES, S. J. Action of amines on phthalic acid, 1319; derivatives of camphoroxalic acid.-XIII.. 1499
TINGLE, J. B. and BRENTON, B F. P. Action of amines on phthalic acid.-VI 113
Titanifluorides, reduction of, by alkali metals...................................... 331
Titanium, metallic, 330; rapid and accurate method for the determination of, 957; properties.. 335
Titanium dioxide, reduction of, by carbon... 332
Titanium tetrachloride, reduction of, with sodium................................... 333
Tolyl ether, bromination of.. 1285
1-p-Tolyl-2-methoxymethylthiourea.. 1284
TORREY, H. A. and CARDARELLI, E J. Some derivatives of 2-acetyl-naphthol-1............. 1477
TORREY, H. A and RAFSKY, H. R. 1-Benzoylphenyl-3-methyl-5-pyrazolone..........1489, 1490
TORREY, H. A. and SUMNER, J B Note on some properties of piperonyloin 1492
TOWER O. F. The precipitation of the iron group and the composition of certain ferric formates.. 953
TOWER, W. S. The Story of Oil (book).. 253
TOWNSEND, C. F. Chemistry for Photographers (book)................................. 1699
TOWNSEND, J. S. The Theory and Ionization of Gases by Collision (book) 1540
Transference experiments with thallous sulphate and lead nitrate 1555
Transference measurements in sodium hydrogen sulphate solutions..................... 1151
Transference numbers, theory of the determination of, by the method of moving boundaries .. 862
TRAUBE, M. See Mengarini.
TREADWELL, F. P. Quantitative Analysis (book)....................................... 1112
TRIER, G. See Winterstein, E.
1,2,5-Trimethylcyclopentanol-1... 1065
Trimethyl-p-nitrophenylethylammonium iodide.. 770
Trinitrophenyl ether... 1292
TRNKA, R. Die physikalischen Eigenschaften des Bodens (book).......................... 576
TRÖGELE, F. Ueber das Verhalten der Alkaloide in den Organen der Atropa belladonna L. (book) 1540
TROY, H. C. See Publow, C. A.
TSCHIRCH, A. Handbuch der Pharmakognosie (book).................................... 1010
Tungstates, note on the paper entitled "Some Organic Tungstates"....................... 541
TURRENTINE, J. W. On the oxalates of hydrazine...................................... 579
TUTTON, A. G. H. Crystalline Structure and Chemical Constitution (book)................. 576

UHLENHUTH, P. and WEIDANZ, O. Praktische Anleitung zur Ausführung des biologischen Eiweissdifferenzierungsverfahrens mit besonderer Berücksichtigung der forensischen Blut-Fleischuntersuchung sowie der Gewinnung präzipitierender Sera (book).................. 253
UHLENHUTH, X. Untersuchungen über "Antiformin," ein bakterienauflösendes Desinfektionsmittel (book)... 253
Ultramicroscopic observations, some colloid-chemical aspects of digestion with............. 680
UNDERBERG, G. Le diamidophenol acide en photographie (book)........................... 896
University of Illinois section.............................Pr. 4, 46, 57, 64, 85 126
URBAIN, G. See Clarke, F. W.
Uric acid, elimination of, following copious water drinking between meals............... 1686

Valence, electron conception of, 1637; partial.. 1650
Vanadium, atomic weight...260, 1114, 1603

Vandevelde, A. J. J. Eléments de chimie générale; préparatoires a l'études biochimique des fermentations (book)........ 430

Van Haagen, W. K. Halides of tantalum........ 729

Vapor densities, apparatus for measurement of, of easily volatil substances........ 1624

Vapor pressure, determining molecular weights of solutes by lowering of, 1615; dynamic method for measuring, with application to benzene and ammonium chloride, 1448; identity of, as determined by the static and by the dynamic methods, 1623, of a pure substance, 471; of calomel, 1546; redetermination of the vapor pressures of mercury from 250° to 435°, 1434; static method for determining the vapor pressures of solids and liquids, 1412; studies in........897, 907, 1434, 1448 1541

Vapors, of organic compounds, action of magnesium upon........ 388

Vases, composition of some Greek........ 2591

Vermorel, V. and Dantony, E Utilisation des sous-produits de la vigne et du vin (book).... 1699

Vinson, A. E. The stimulation of premature ripening by chemical means........ 208

Vogel, E. Taschenbuch der Photographie. Ein Leitfaden für Anfänger und Fortgeschrittene (book)........ 253

Vogel, H. W. Photographie (book)........ 253

Voigt, M. Beiträge zur Oxydation des Phosphors im basischen Konverter (book)........ 1366

Volatilization of sulphuric acid when precipitates are heated........ 597

Volatil substances, apparatus for measurement of vapor densities of........ 1624

Vorbrodt, J. See Bruner, L

Vortmann, G. Uebungsbeispiele aus der quant. chem. Analyse (book)........ 1366

Vrancken, E and Aulard, A. Manuel de la fabrication du sucre de betterave a l'usage des praticiens (book)........ 253

Wadleck. Theorie und Praxis des Generatorbetriebes (book)........ 1010

Wadsworth, M. E. Crystallography· An Elementary Manual for the Laboratory (book)...... 576

Waidner, C W. and Burgess, G. K. Platinum Resistance Thermometry at High Temperatures (book)........ 1112

Walden. Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge (book)........ 1700

Waldheim, M v Nach Autoren und Sachnamen geordnete Sammlung der wichtigsten Reagenzien und Reaktionen für Chemie, Pharmazie, Physiologie usw. 3 (book)........ 1366

Wallace, R C. Ueber die binären Systeme des Natriummetasilicats mit Lithium-, Magnesium-, Calcium-, Strontium-, und Bariummetasilicat (book)........ 1540

Wallach, O Tabellen zur chemischen Analyse (book)........ 1366

Ware, F C. See Renshaw, R R

Warren, W. H An apparatus for absolute alcohol........ 698

Washburn, E. W. A simple system of thermodynamic chemistry based on a modification of the method of Carnot, 467, 1636, the fundamental law for a general theory of solutions.653, 1636

Washington section........Pr 8, 47, 60, 67, 82, 68, 124, 130

Washington, H. Manual of the Chemical Analysis of Rocks (book)........ 1112

Water, composition of sea, near Beaufort, N C, 646; determination of ammonia nitrogen in, in the presence of hydrogen sulphide, 1256; destruction of invertase by, 985, determination of nitrates in, 630; ionization of, at 100 and 156°, 168; ionization of, at 218 and 306°, 172; ionization of, at high temperatures, 159; surface energy of........ 1169

Water drinking, studies on (uric acid elimination following copious water-drinking between meals)........ 1686

Watermelon seed, chemical examination of........ 360

Waters, C. E. A convenient potash bulb (note)........ 1691

Weber, C. O. The Chemistry of India Rubber (book)........ 896

Wedekind, E. and Lewis, J Neue Atomgewicht-Kurven (book)...... 814

Weidanz, O. See Uhlenhuth, P

Weight, concerning the correction of the apparent weight of a salt to the vacuum standard.... 507

Weil, S. F. Ueber Asphalt- und verwandte Industrien (book)........ 1540

Wein, E. Das Kalisilicat (Phonolithmehl) als Kalidüngemittel (book)........ 253

Weinstein, B. Physik und Chemie in gemeinverständlicher Darstellung. Zum Selbstunterricht und für Vorlesungen (book)........ 253

Weisbach, A. Tabellen zur Bestimmung der Mineralien mittels ausserer Kennzeichen (book).. 253

Wells, E. E. See Spear, E. B.

Wentzel, und Paech. Photographisches Reisehandbuch (book)........ 253

Werner, A. Neuere Anschauungen auf dem Gebiete der anorganischen Chemie (book), review.. 1695

Western New York section.... Pr. 5, 90, 123 130

Wheeler, A. S. Composition of sea water near Beaufort, N. C., 646; the instability of alloxan (note).... 809

Wheeler, A. S. and Oates, W. M. The bromination of anthranilic acid.... 770

Wheeler, H. J. Charles Anthony Goessmann (obituary).... Pr. 131

White, A. S. Logic of Nature (book).... 1010

Whitney, M. Fertilizers for Wheat Soils (book).... 1540

Whitney, W. R. Organization of industrial research, 71; some chemistry of light (address).... 147

Wickenden, W. E. Illumination and Photometry (book).... 896

Wiechowski, S Einführung in die qualitative chemische Analyse zum Gebrauch bei den prakt. Uebungen im Laboratorium (book).... 253

Wieland, H. Die Knallsaure (book).... 576

Wien, W. Ueber Elektronen (book).... 430

Wiener, O. Ueber Farbenphotographie und verwandte naturwissenschaftliche Fragen (book).. 254

Willard, H H. See Richards, T. W.

Williams, R. Essentials of Chemistry (book).... 1700

Wilson, J. H. See Richards, T.

Winterstein, E and Trier, G. Beilsteins Anleitung zur qualitativen Analyse (book), 254; Die Alkaloide. Eine Monographie der natuerlichen Basen (book), review 1696, title.... 1540

Wisconsin section.... Pr. 7, 45, 60, 82, 88, 93, 124 130

Wise, L. E See Bogert, M. T.

Withrow, J. R. See Hughes, J. S

Witt, O. N. und Lehmann, L. Chemische Technologie der Gespinstfasern, ihre Geschichte, Gewinnung, Verarbeitung und Veredlung (book).... 1010

Wodiska, J. Book of Precious Stones Identification of Gems and Gem Minerals and Account of their Scientific Commercial, and Artistic Aspects (book).... 814

Wohl, A. Organische Chemie und die Lehre vom Leben (book).... 1112

Wolf, K. Grundzüge der Elektrotechnik zum Gebrauche an gewerblichen Lehranstalten (book).... 430

Wolff, J. Contribution à la connaissance de divers phénomènes oxydasiques naturels et artificiels (book).... 1540

Wolk, D. Contribution a l'étude de l'azoture d'aluminium et de l'azoture de baryum (book). 1366

Wolland, H. Chemisches Praktikum (qualitative Analyse) für höhere Lehranstalten (book).. 254

Woodman, A G. See Richards, E. H.

Woodward, C. J. Five-figure Logarithms and Tables for Chemists (book).... 1112

Wool grease, hydrocarbons of the wool grease oleins.... 1071

Worden, K. Monographien über angewandte Elektrochemie. XXXI. Electrolytische Zahler (book).... 254

Wüst, F. Mitteilungen aus dem eisenhüttenmännischen Institut der Klg Techn Hochschule Aachen (book).... 1010

Wyssozky, W. F. Ueber die Bindung der Derivate des Jods an das Gewebe der Leber (book).. 1540

Xylenes, heats of combustion of the.... 268, 293

1,3,4-Xylidylcamphoformenaminecarboxylic acid, 1503, 1512; xylidine salt.... 1503, 1511

Yttrium, basic nitrate of.... 873

Zerr, G. und Rübencamp, R. Handbuch der Farbenfabrikation (book).... 254, 1700

Zetzsche. Mikrophotographischer Atlas der industriellen Faserstoffe (book).... 576

Zimmermann, W. Moderne Batistfarben (book).... 1366

Zinc, electrolytic determination of, 530, 533, 1632; heat of solution of.... 456

Zsigmondy, R. Colloids and the Ultramicroscope (book).... 254

Zwick, H. Hydraulischer Kalk und Portlandzement, ihre Rohstoffe, physikalischen und chemischen Eigenschaften (book).... 254

PROCEEDINGS

OF THE

American Chemical Society

FOR THE YEAR 1910

EASTON, PA.:
ESCHENBACH PRINTING COMPANY
1910

PROCEEDINGS.

Contents.

January.

Council 1
Members Elected between November 15th and December 15th 1
Board of Directors 2

Meetings of the Sections:

Univ. of Missouri Section 3
Sodium Benzoate and the Referee Board, P. F. Trowbridge. The Detroit Meeting of the American Chemical Society, P. K. Francis. The Winnipeg Meeting of the British Association for the Advancement of Science, H. Schlundt. Factors which Influence the Digestibility of Feed, P. F. Trowbridge. Explosive Antimony, R. C. Palmer. Synthesis of Pyrimidine, R. B. Gibson.
Indiana Section 3
The Relation of Radioactivity to the Other Sciences, R. B. Moore. A Study of the Preparation and Preservation of Crushed Fruit and Fruit Syrups, I. L Miller. Some Analyses of Tomato Catsup, H. E. Bishop. (*a*) Temperance Beers. (*b*) Estimation of Dextrose, Dextrin and Maltose, H. E. Barnard.
Chicago Section 4
The Electric Theory of Oxidation and Reduction, J. Stieglitz.
University of Illinois Section 4
The Determination of Nitrogen by the Kober Method, F. W. Gill. (1) The Relation of the Water Supplies to the Typhoid Fever Death in Illinois. (2) A New Thermo-regulator for Incubators, E. Bartow.
Philadelphia Section 4
Legal Aspects of Chemistry—symposium. The Work of the Expert Witness, S. P. Sadtler. Textile Problems and Disputes, F. Dannerth. The Legal Side of Toxicology, M. Bearwood. The Enforcement of the Food and Drugs Act, C. S. Brinton. The Purification of Water by Ozone with Remarks on the Commercial Production of Distilled Water, H. Leffmann. The Jedun Vacuum Evaporator and its Application to By-products, A. P. Smith. Mondia Milk, A. E. Kitson
Louisiana Section 4
Manufacture of White Lead from Galena, Mr. McGee.
Section of Western New York 5
Estimation of Small Quantities of Arsenic, by Sanger's Modification of the Gutzeit Test, W. H. Watkins. The Action of Bacteria on Minerals, G. Morgan. Color in Preserved Fruits after Treatment with Lead Subacetate. New Sanitary Regulations in Raising and Shipping Oysters, W. L. Dubois. Microphotographs of Fine Points and Fibers, Mr. Morey. Errors in the Analyses of Linseed Oils, G. H. Pickard. Some Delicate Pycnometers and Glass Pens, R. E. Fowler. Vanadium in Chrome Iron Ore. Periodic Phenomena in the Aluminum Electrolytic Rectifier, R. Phillips.
Nebraska Section 5
Universities I Have Visited, C. S. Avery. The Reaction of the Blood, C.

F. Crowley. Studies in Asphalt, C. J. Frankforter. Some Notes on the Meeting of the British Association, F. J. Alway. Systematic Separation and Detection of the Common Acids, O. L. Barnebey.

Cornell Section 5
The Measurement of High Temperatures by Various Pyrometers, J. S. Shearer. Disposal of Sewage, H. N. Ogden.

Northeastern Section 6
The Bio-chemistry of Nucleic Acid, P. A. Levene. Alkali-insoluble Phenols, H. A. Torrey.

Kansas City Section 6
Benzoate of Soda Discussion, E. H. S. Bailey. Practical Advantages of Drying Alfalfa by Artificial Heat, R. E. Shuey.

Rhode Island Section 6
The Influence of Sodium and Potassium Salts upon the Subsequent Yield of Potato Tubers Planted under Like Manurial Conditions, H. J. Wheeler.

Milwaukee Section 7
High Temperatures and Other Measurements, O. Kowalke.

Georgia Section 7
Studies in the Sampling of Mixed Fertilizer, Size of Sample to be Taken, F. B. Porter. The Early History of the Cement Industry, C. N. Wiley. The Honey Locust as a Cattle Food, C. A. Wells. A Triumph of Chemistry Over Bacteriology in the Test of Polluted Waters, H. B. Arbuckle. An Investigation of the Stain of the Black Walnut on the Fish of Our Streams, G. P. Shingler.

Louisville Section 7
Fast Colors on Cotton, C. E. Martin.

Cincinnati Section 7
Some Experiments Illustrating Certain Phases of the Electrolytic Dissociation Theory, L. W. Jones.

Wisconsin Section 7
The Industrial Methods of Obtaining Resinous Products from the Southern Yellow Pine, L. F. Hawley.

Washington Section 8
Estimation of Glycerine in Meat Preparations, F. C. Cook. Enzymes and their Relation to Soil Fertility, M. X. Sullivan. Detection of Colocynth in Powdered Colocynth, V. K. Chesnut.

Lehigh Valley Section 8
The Relation of Economic Products and Geology in the Lehigh Valley, B. L. Miller. A Chemist's Slide Rule, R. K. Meade. Decomposition Temperature of Some Sulphates, W. S. Landis.

Cleveland Section 8
The Commercial Manufacture of Oxygen, C. F. Brush. The Brick Industry in Cleveland, F. K. Van Horn.

Minnesota Local Section 8
The Reaction between Ammonium Chloride and Potassium Dichromate when Heated, G. B. Frankforter, V. H. Roehrich and E. V. Manuel. The Nu-Cleation of Mixed Vapors in Dust-free Air, I. H. Derby and E. X. Anderson.

Deceased Members 8

February.

Minutes of the Forty-first General Meeting of the American Chemical Society... 9
Report of the Secretary for 1909. Report of the Editor of the Journal of the American Chemical Society and Chemical Abstracts. Report of the Journal of Industrial and Engineering Chemistry for the Year 1909. Treasurer's Report. Also reports of the Finance Committee of the American Chemical Society for the Year 1909, Librarian for the Year 1909. Division of Industrial Chemists and Chemical Engineers. Division of Physical and Inorganic Chemistry. Division of Fertilizer Chemistry. Division of Agricultural and Food Chemistry. Division of Organic Chemistry. Division of Pharmaceutical Chemistry. Section of Chemical Education. Section of Biological Chemistry. India Rubber Chemistry Section.
Council.. 30
Boston Meeting.. 30
Resolutions on the Death of Charles Benjamin Dudley.............. 32
Report of the Paper Committee of the American Chemical Society 32
Budget for 1910 38
Members Elected between Dec. 15, 1909 and Jan. 15, 1910.............. 40
Board of Directors 44
Meetings of the Sections:
Pittsburgh Section 44
Some Improved Gas Analysis Apparatus, E. J. Hoffman. The Determination of the Percentage of Phosphorus Retained with the Ferric Chloride in the Ether Separation, R. J. Wysor. The Analysis of Explosives, W. O. Snelling.
Section of Eastern New York 44
The Natural Resources of New Zealand, M. A. Hunter The Hydrate Theory of Solutions, A. T. Lincoln Recent Advances in the Liquefaction of Gases, C. F. Hale.
Wisconsin Section... 45
The Utilization of the Amino Acids and Polypeptids bv the Tubercle Bacillus, W. F. Koelker.
Indiana Section.. 45
Concerning the Decomposition of Uric Acid by Enzymes, C. E. May. Boiler Water in Railway Service, J. R. Francis. Scientific Treatment of the Problem of Cutting a Brilliant of Any Transparent Material, F. B. Wade. Morphine Determinations, A. D. Thorburn.
Iowa Section... 45
The Estimation of Cobalt and Arsenic in Smaltite, Nicholas Knight. Nitrogenous Excretion, S. Hartzell. Metalluric Tellurites, E. Wolesensky. Delicate Tests for Cobalt in the Presence of Nickel and Iron, W. J. Karslake. Colloidal Solutions, J. N. Pearce. Bleaching of Flour, E. W. Rockwood.
St. Louis Section.. 46
The Relation of Chemistry and Chemical Engineering to the Conservation of Our Natural Resources, H. E. Wiedemann. Timber Preservation, A. L. Kammerer, E. K. Fulks.
Louisiana Section.. 46
Waste Products, J. C. Mims.
New York Section... 46
Analyses of Some Antique Bronzes, M. Loeb and L. R. Morey. The Action of Radium Salts upon Ruby, C. Baskerville. Apparatus for Drying Flasks,

C. Baskerville and Reston Stevenson. The Origin of the Chemical Elements, H. R. Russell. Chemical Examination of Watermelon Seed, and Chemical Examination of Pumpkin Seed, F. B. Power and A. H. Salway. Further Researches in the Quinazoline Field, C. G. Amend and M. T. Bogert.
University of Illinois Section.. 46
The Heat of Solutions of Metals in Acids, L. L. Burgess. The Effect of External Conditions upon the Physiological Activities of Some De-nitrifying Organisms, J. H. Petit.
Syracuse Section.. 47
Invertase, C. S. Hudson. Some New Electro-chemical Processes, E. H. Archibald. An Electric Gas Meter, E. C. Scott. Report of the Recent Convention of Chemical Engineers, W. M. Booth. The Electrical Theory of Oxidation and Reduction, J. Stieglitz.
Cincinnati Section.. 47
Chemical Theories, J. Ellms.
Washington Section.. 47
Nitrification in Soils, K. F. Kellerman, E. R. Allen and I. G. McBeth. Availability of Iodophenin in the Separation of Acetanilid and Acetphenetidin, W. O. Emery. Translocation of Plant Food during Germination of Wheat, J. F. Breazeale.
Deceased Members.. 47

March.

Council.. 51
Members Elected between January 15th and February 15th.
Meetings of the Sections:
Puget Sound Section.. 56
Some Non-Ionic Reactions, W. M. Dehn. The Status of Powdered Coal as a Fuel, D. C. Farnham.
Chicago Section.. 56
The Council on Pharmacy and Chemistry and the Chemical Laboratory of the American Medical Association. W. A. Puckner. The Electrolytic Theory of Corrosion and an Amendment Thereto, W. D. Richardson.
North Carolina Section.. 56
Chemistry of Commercial Feeds, G. M. MacNider. The Determination of Flax Seed Products by the Specific Gravity Method, C. H. Herty and E. J. Newell. Caffiene in Our Beverages, E. V Howell. A Comparison of the Foster, the Tagliabue and the New York Board of Health Oil Testers, M. Orr. Application of Physical Chemistry to the Study of the Oleo-Resins, C. H. Herty. Bromination of Anthranilic Acid, A. S. Wheeler and W. M. Oates. Nature of Attractive Forces, J. E. Mills. The Delicacy of the Diphenylamine Test for Nitrates and Nitrites, W. A. Withers and B. J. Ray.
Cornell Section.. 57
Further Contributions to the Chemistry of the Phenolsulphonic Acid Method for Nitrates, D. S. Pratt. Ammonolysis of Hydrazine Sulphate, T. W. B. Welsh. Electrolytic Corrosion of Some Metals, G. R. White. The Influence of the Basicity of the Soil and of the Growth of Legumes on the Availability of Soil Nitrogen, T. L. Lyon. Report of the Boston Meeting, A., W. Browne.

Kansas City Section ... 57
Food Law and the Jobber, R. Hirsch. Food Law and the State, H. L. Jackson.
University of Illinois Section ... 57
Atomic Weight of Phosphorus, G. Jones. Adiabatic Determination of Heat of Combustion, R. H. Jesse, Jr. The Atomic Weight of Tantalum, C. W. Balke. A Measure of Thermodynamic Positivity and Negativity, C. G. Derick.
Pittsburg Section ... 57
The Manufacture and Analysis of Smokeless Powder, C. G. Storm. Results of Laboratory and Field Inspection of Various Painting Tests, H. A. Gardner.
Philadelphia Section ... 58
The Cause of Color in Plants, H. Kraemer. The Extraction of Gold from Sea Water, A. W. Comey. Is there Caramelization in Riva's Test, D. W. Horn. The Application of the Jet in Chemical Processes, O. Nagel. The Chemistry of the Tariff of 1909, C. C. Roberts.
Rhode Island Section ... 58
The Structure of Retene and its Relation to Some Natural Resins, J. E. Bucher.
Louisiana Section ... 58
The Causes of Variations in Sugar House Results, L. A. Becnel.
Northeastern Section ... 59
Color Photography at the Present Time, L. Derr.
University of Missouri Section ... 59
Glycogen Content of Beef Flesh, C. K. Francis. Apparatus for Measuring the Comparative Hardness of Fat or Similar Substances, E. A. Perkins.
Milwaukee Section ... 59
Iron and Steel, R. S. MacPherran Lead Smelting, B. L. Salomon.
California Section ... 59
The Bearing of Recent Work in Radioactivity on the Atomic Theory, E. C. Franklin.
Louisville Section ... 59
Reducing Oils for Paints, R. C. Lord. The Detection of Alumina in Water, W. H. Lovejoy. The Purchase of Coal on the B. T. U. Basis, A. M. Breckler. Gravimetric Determination of Reducing Sugars, F. F. Hasbrouck.
Cincinnati Section ... 60
The Interpretation and Value of Physical and Chemical Tests in the Control of Water Purification Plants, C. Bahlmann. The Biological Features of Water Purification at Cincinnati, Ohio, L. G. Gedesche.
Washington Section ... 60
Solubility of Gold in Nitric Acid, F. P. Dewey. The Detection of the Deterioration of Corn with Special Reference to Pellagra, C. L. Alsberg and O. F. Black.
Wisconsin Section ... 60
The Separation of Curd from Butter Milk, J. L. Sammis. The Importance of Metabolic Water in the Development of Living Organisms, S. M. Babcock.
New York Section ... 60
Nucleic Acids, P. A. Levene. Determination of Sodium Chloride in Milk, P. Poetschke. Some Colloid-chemical Aspects of Digestion, with Ultra-

microscopic Observations, J. Alexander. The Fate of Amino Acids in the Organism, G. Lusk.
Syracuse Section........ 60
The Chemist and the Community, A. D. Little. The Conference of the Sections, H. C. Cooper. The Chemist's Place in Industry, A. D. Little.
Section of Eastern New York........ 61
Modern Bacterial Methods of Sewage Treatment, L. P. Kinnicutt.
Minnesota Local Section........ 61
Deceased Members........ 61
San Francisco Meeting........ 62

April.

Council........ 63
Members Elected between February 15th and March 15th.

Meetings of Sections:

University of Illinois Section........ 64
Application of the Rare Earths to Incandescent Lighting, H. S. Miner. The Atomic Weight of Tantalum, C. W. Balke. A Measure of Thermodynamic Negativity and Positivity, C. G. Derick. Equilibrium between Amalgam and Amalgam Solutions, G. McP. Smith. The Alkylation of Cyanacetic Ether, J. C. Hessler. Opalescence and the Function of Boron in the Glaze, R. T. Stull.
Indiana Section........ 64
A Simple Method for Determining the Relative Strength of Acids and the Relative Strength of Bases, W. M. Blanchard. Some Problems in Iron Analyses, H. A. Schwartz. The Rare Earths and their Use in Incandescent Gas Mantles, H. S. Miner. Laboratory Notes, H. A. Duden. Laboratory Kinks, R. P. Noble.
Puget Sound Section........ 65
Mineralization of Some American Waters, R. B. Dole.
St. Louis Section........ 65
The Action of Magnesium upon the Vapors of Organic Compounds, E. H. Keiser. The Extraction of Glycerine from Soap Lye, C. B. Cluff.
Louisiana Section........ 65
Personal Experiences in South African Gold and Diamond Mines. T. L. Carter. Chemical Examination of Imported Merchandise, W. L. Howell. Some Notes on the Assay of Tincture of Nux Vomica, G. B. Taylor.
Kansas City Section........ 66
The History of the Development of the Elements, F. B. Dains. The Chemical Control of a Soap and Glycerine Factory, M. Brayton Graff.
Cornell Section........ 66
Problems of the Gas Engineer, C. F. Hirshfield. The Chemical Resources of the United States, J. E. Teeple.
Rhode Island Section........ 66
Field Notes from the Natural History of Silica, C. E. Swett. The Testing of Explosives for Use in Coal Mines with Special Reference to the Prevention of Mine Disasters. C. E. Munroe.
Chicago Section........ 67
Problems of the Linseed Oil Industry, O. Eisenschiml.
Northeastern Section........ 67
Present Conception as to the Constitution of Matter, D. F. Comstock. Production of Incandescent Mantles and Chemicals, M. C. Whitaker.

Washington Section.... 67
The Construction and Equipment of a Chemical Laboratory, W. D. Bigelow.
Syracuse Section.... 67
The Manufacture and Testing of Refractory Material, A. V. Bleininger.
Section of Eastern New York 67
Wireless Telegraphy and Telephony, W. J. Williams.
New York Section.... 67
The Determination of Copper in Blister and Refined Copper, W. C. Ferguson. Scrubbing Device for Vacuum System in the Laboratory, C. Baskerville. Rack for Holding Reagents in Bulk, J. L. Sporer. An Improved Ethylene Generator, V. L. King. A Constant Temperature Drying Oven and Gas Regulator, H. T. Beans. An Automatic Pipette, S. H. Beard. Description of a Modified Pettersson and Palmquist Apparatus, C. T. G. Rogers. Tests of Iron Wire for Standardization Purposes, C. H. Stone and C. E. Cheeseman.
California Section.... 68
The Electrical Precipitation of Suspended Matter, F. G. Cottrell.
Cincinnati Section.... 68
A Journey through the Navajo and Mogui Indian Countries, J. U. Lloyd.
Philadelphia Section.... 68
The Evidence Obtained during the Past Twelve Years for the Solvate Theory of Solutions, H. C. Jones.
Minnesota Section.... 68
The Chemical Replacement of the Metals by Each Other, L. Kahlenberg.
Deceased Members.... 69
Eighth International Congress o Applied Chemistry.... 75
Gmelin-Kraut's Handbook.... 76

May.

Council.... 77
Members Elected between March 15th and April 15th

Meetings of the Sections

Indiana Section 79
Glass Sands and Ball Clays of Florida, H H. Buckman. On the Purpose and Methods of the Chemistry Course in the Public School, F B. Wade. The Teaching of Chemistry in the University, J. H. Ransom.
St. Louis Section.... 79
Chemistry in America and Germany. Electrolytic Preparation of Hydrazine, R. F. Weber. Terpineless Extract of Lemon and Analysis Thereof, S. H. Baer. A Rapid Method of Estimating Iron in Iron Ores, L. McMaster. Ozone in Water Treatment, W. F. Monfort.
Chicago Section.... 80
The Chemist in a Brass Foundry, W. M. Corse The Borax Industry, the Mining and Manufacture of Borax and its Uses. The Development of the Borax Industry in California and Nevada, and Sources of Supply in Other Countries, S. T. Mather. Mining and Refining of Borax, F. M. Dupont. The Use of Borax in Manufacturing Enameled Sanitary Ware, C J. Wolff. The Use of Borax in Manufacturing Enameled Kitchen Ware, H. Coonley.
Nebraska Section.... 80
Present Status of the Bleached Flour Controversy, F J. Alway. Analysis of Soaps, S. H. Ross. Nitrogen Problems and Dry Farming, R. S. Trumbull. Determination of Humus, E. K. Files.

Louisville Section.. 80
Antitoxins, L. A. Brown. Liquid Mixtures of Constant Boiling Point, G. Ryland. Possible Variation in the Composition of Distiller's Dried Grains, A. M. Peter. Operation of the Louisville Filter Plant, W. H. Lovejoy. Bacteriological Examination of Water, F. M. Scales.
Milwaukee Section.. 81
The Methods of Production and Properties of the Chemical Dry Colors, C. H. Hall.
Rhode Island Section 81
Some Problems of the Testing Laboratory, W. H. Kenerson.
New York Section.. 81
Notes on the Determination of Essential Oils, F. D. Dodge. General Outline of the Leather Industry, A. Rogers. The Process of Bating, A. A. Claflin. Vegetable Tanning Materials, J. H. Yocum. Recent Advances in Chrome Tannage, O. P. Amend. The Coloring of Leather, F. E. Atteaux. Oils Used in the Leather Industry, E. A. Prosser.
Section of Eastern New York 81
Usefulness of Chemistry in Sanitation, H. W. Wiley.
Cincinnati Section 82
(*a*) Salt. (*b*) Yellow Fever, A. Springer.
Wisconsin Section.. 82
Some Chemical Problems of the Forest Products Laboratory, H. S. Bristol.
Washington Section 82
The Effect of Drugs and Diet upon the Thyroid, R. Hunt. Contribution to the Knowledge of Phosphoric Acids, B. Herstein and P. F. Kebler. Separation and Determination of Cocaine and of Atropine from Strychnine, H. C. Fuller.
Louisiana Section.. 82
Food in Light of Modern Chemistry, G. Mann.
Minnesota Section.. 82
A Correction in the Beckmann Thermometer Due to the Hydrostatic Pressure of the Mercury Column, I. H. Derby. Comparison of Rapid Electroanalytical Methods: Part 1, the Determination of Copper, F. C. Frary and A. P. Peterson.
Deceased Members.. 82

June.

Council.. 83
Members Elected between April 15th and May 15th.
Meetings of the Sections:
University of Missouri Section 84
Changes in Chemical Composition of Salmon during the Spawning Season, C. W. Green. Chemical Composition of Some of the Animals Slaughtered as Human Food. Flesh of Beef Animals, L. D. Haigh. Some New View Points in Organic Chemistry, S. Calvert. Chemistry of the Rare Earths, with Special Application to Incandescent Lighting, H. S. Miner. Alpha Particle, H. Schlundt.
Indiana Section.. 84
Deterioration of Various Drug Extracts, F. R. Eldred. The Coming Revision of the United States Pharmacopoeia, E. G. Eberhardt. The Pharmacopoeia as a Legal Standard in Municipal and State Work, H. E. Barnard.

University of Illinois Section 85
Gas Calorimetry, S. W. Parr. (1) Condensations in the Mesoxalic Ester Series. (2) The Acid Products of the Action of the Red Oxides of Nitrogen on Malonic Esters, R. C. Curtiss. A Comparative Study of the Freezing Points, Conductivities and Viscosities of Aqueous Solutions of Electrolytes Belonging to the Same Ionic Type but Differing in Degree of Hydration, D. A. MacInnes.
Pittsburgh Section 85
Aluminum in Industrial Engineering, E. Blough. Thermochemistry of Explosives, W. O. Snelling. The Explosive Power of Coal Dusts, A Method of Testing, J. C. W. Fraser The Materials Laboratory of the Public Works Department of Pittsburgh, M. S. Evans.
Syracuse Section 86
Road-making Material, C. Richardson.
Kansas City Section 86
Chemistry Fifty Years Ago at Yale, J. T. Lovewell. Some Studies in the Reduction of Aldehydes and Ketones, J. B. Whelan. On the Relative Digestibility of Unbleached and Bleached Flour, J. T. Willard and C. A. A. Utt. Notes on Chemical Topics, F. B. Dains.
Rhode Island Section 86
Chlorine Disinfection of Water and Sewage, F. P. Gorham.
Northeastern Section 86
Electrolysis of Chlorides Theoretically Considered, H. Carmichael.
Milwaukee Section 86
Opaque White Pigments Used in the Manufacture of Paint, F. S. Low.
Iowa Section 86
Some Suggestions on the Determination of Calcium, G. Heise. The Effect of Continued Grinding on Water of Crystallization, N. Knight. Laurolene, W. A. Noyes. The Manufacture of Absolute Ether, L. Andrews. The Modern Manufacture of Portland Cement from the Mechanical and Chemical Standpoint, G. P. Dieckmann. A New Method for the Determination of Humus, A. A. Wells On the Quality of Iowa Deep Well Waters, W. S. Hendrickson. The Efficiency of Land Plaster in Preventing the Loss of Ammonia in Manure, W. W. Scott.
Cornell Section 87
Some New Developments in Limnology, J. G. Needham.
New York Section 87
Electrolytic Theory of Oxidation and Reduction, J. Stieglitz. On the Action of Crushed Quartz upon Nitrate Solutions, H. E. Patten. Estimation of Iodine in Organic Compounds and in the Presence of Other Halogens, A. F. Seeker and W. E. Mathewson. Stilbazoles in the Quinazoline Group, G. D. Beal and M. T. Bogert.
California Section 87
Electrometallurgy of Iron on the Pacific Coast, G. H. Clevenger.
St. Louis Section 87
The Tin Plague, L. R. A. Suppan. A Study of Some Methods Used in Oil Analysis, J. J. Kissler and G. K. Mathiason.
Cincinnati Section 88
Creosote Wood Block, P. F. Wehmer.
Wisconsin Section 88
Processes of Color Photography, J. Howard Mathews.

Washington Section 88

The Exact Determination of Sulphur and of Barium in the Presence of Alkali Salts, I. K. Phelps. The Determination of Nitrogen in the Feces, I. K. Phelps. Oil Cement Concrete, A. S. Cushman. The Complexity of the Humus Extract of Soils, E. C. Shorey. The Separation and Determination of Cadmium in Presence of Copper, E. A. Hill.

San Francisco Meeting 88

July.

Council 89

Members Elected between May 15th and June 15th.

Meetings of the Sections:

Section of Western New York 90

Cements, Ancient and Modern, G. M. J. MacKay. The Microscope in the Chemical Laboratory, E. M. Chamot.

Columbus Section 91

The Recent Developments in the Examination of Proprietary Remedies, C. A. Dye. Phosphorescence of Some Inorganic Salts, J. Wilkinson. Experimental Study of the Metabolism of the Purins in the Mammalian Organisms. J. F. Lyman.

University of Missouri Section 91

Louisville Section 91

Colloids, R. N. Maxson. Theory of the Continuous Still, A. M. Breckler. Kentucky Clays, J. S. McHargue.

Philadelphia Section 92

The Chemistry of the Suprarenal Gland, C. E. Vanderkleed. Analysis of Ground Cloves, A. T. Collins.

Chicago Section 92

Symposium on Soap. Special Points to be Considered in the Analysis of Soaps, W. H. Low. The Work of the Glycerine Committee of the American Chemical Society, A. C. Langmuir. Glycerine Analysis, R. E. Divine. The Pears Soap Case: Detection of Volatile Substances in Soaps, E. M. Slocum The Manufacture of Glycerine by the Garrigues Process, G. A. Moore. Historical Review of Saponification Processes, W. D. Richardson.

Louisiana Section 92

The Corrosion of Iron, B. P. Caldwell. Chemical Technology in Louisiana.

Kansas City Section 92

Chemistry and Cupola Practice, W. W. Cox. Salt Rising Bread, H. A. Kohman.

Section of Eastern New York 93

Accuracy in Certain Difficult Determinations, E. W. Morley. The Products of Milk. Junket Tablet, J. D. Frederiksen. Milking Machines and Milk Separators, L. Burrell.

Rhode Island Section 93

Some Recent Researches in High Vacuum, F. G. Keyes.

Wisconsin Section 93

Nebraska Section 93

Utilization of Waste Wood with Some of its By-Products, G. B. Frankforter.

Cornell Section 93

Fractional Crystallization of the Rare Earths, C. W. Bennett. Fractionation of the Rare Earths, H. N. Frear. Temperature Measurements in the

Carborundum Furnace, H. W. Gillett. Electrolysis of Certain Liquid Ammonia Solutions, M. E. Holmes. Sugar and Alcohol in Apple Waste, B. J. Lemon. Sulphated Storage Cells, G. A. Perley.
Georgia Section 94
The Volumetric Determination of Phosphoric Acid by Precipitation in the Cold, W. P. Heath. The Halides of Tantalum, W. K. Van Haagan. Soil Fertility, F. B. Porter.
New York Section 94
The Examination of Ethyl Ether, C. Baskerville and W. A. Hamor. An Examination of Present Methods of Determining Diastatic Power, H. C. Sherman, E. C. Kendall and E. D. Clark. A Study of the Action of Pancreatic Amylase, E. C. Kendall and H. C. Sherman. A Case of Iron Corrosion, F. J. Pond. A Note on the Constancy of the Solubility Product, A. E. Hill.
Deceased Members 94

August.

Council 95
Members Elected between June 15th and July 15th.
Board of Directors 95
Meetings of the Sections:
Puget Sound Section 96
Some Chemical Curiosities, H. G. Byers. Some Notes on the Installation and Operation of the 60-Ton Refuse Destructor at Lake Union, C. J. Moore.
St. Louis Section 97
The National Pure Food Law, D. B. Bisbee.
Syracuse Section 97
Deceased Members 97

September.

Minutes of the Forty-Second General Meeting of the American Chemical Society 99
Council 105
Members Elected between July 15th and August 15th.
Meetings of the Sections:
Minnesota Section 111
The Diffusion of Oxygen through (*a*) Organic Liquids, and (*b*) Solids, G. B. Frankforter, G. W. Walker and R. S. Callaway. Influence of Traces of Iron, Lead and Copper on the Color of Cadmium Sulphide, G. B. Frankforter and J. G. Dietrichson.
Philadelphia Section 111
Modern Electro-Chemical Analysis, E. F. Smith.
North Carolina Section 111
Colloidal Chemistry, Duncan MacRae. The Unsaturated Character of the Resins of *Pinus Sabiniana*, C. H. Herty and E. N. Tillett. The Specific Heat of Benzol and its Saturated Vapor, J. E. Mills and D. MacRae. The Bleaching of Flour by Nitrogen Peroxide, W. M. Allen. The Effect of Acids on Ethyl Phospho-Platino-Chloride, C. H. Herty. The Specific Heat of Carbon Tetrachloride and its Saturated Vapor, J. E. Mills and Duncan MacRae. A Study of the Resene of *Pinus Hetrophylla*, C. H. Herty, W. A. Houck and T. P. Nash.
Milwaukee Section 112
Rhode Island Section 112

October.

Council 113
    Members Elected between August 15th and September 15th.
Deceased Members 113
Willard Gibbs Medal 120

November.

Division of Agricultural and Food Chemistry 121
Council 121
    Members Elected between September 15th and October 15th.
Board of Directors 121
Meetings of the Sections:
    Chicago Section 122
        Milk. (1) Toxicity of Milk and Milk Serum, E. Gudeman. (2) Cost of Production of Milk, J. P. Grier. (3) Cost of Distribution of Milk, H. R. Ryder. (4) Condition of the Chicago Milk Supply, D. T. Gunning.
    Section of Eastern New York 122
        Reminiscences of Nernst, E. Ellery. The San Francisco Meeting of the American Chemical Society, W. R. Whitney. Recent Researches in Inorganic Chemistry, M. A. Hunter.
    Section of Western New York 123
        Functions of the American Chemical Society, Pres. Watkins.
    Rhode Island Section 123
        Protective Coatings for Various Structural Materials, H. A. Gardner.
    New York Section 123
        The Position of the Chemist in the Commonwealth, C. Baskerville. International Congresses, C. Baskerville. The Eighth International Congress of Applied Chemistry, W. H. Nichols. The American Chemical Society and the Eighth International Congress of Applied Chemistry, B. C. Hesse. The Polyiodides of Potassium, C. L. Parsons. The Trip of the American Chemical Society to San Francisco, L. H. Baekeland.
    Louisville Section 124
        Road Oils, R. M. Parks. Standard Samples, W. E. James. Determination of Phosphoric Acid in Vinegars, F. F. Hasbrouck.
    Wisconsin Section 124
        Terpenes as Oxygen Conveyers, E. Kremers.
    Washington Section 124
        The Mechanism of a Peroxidase Reaction, H. H. Bunzel. Biophotogenesis, F. A. McDermott.
    Syracuse Section 124
    Indiana Section 124
        The Rare Gases of the Atmosphere, R. B. Moore.
    California Section 124
        The Troubles of a Cannery Chemist, W. Antoni.

December.

Council 125
    Members Elected between October 15th and November 15th.
Meetings of the Sections:
    St. Louis Section 126
        Fire Clay and Some of its Properties, R. F. Weber.

University of Illinois Section 126
  Natural Gas as a Source of the Rare Gases, D. F. McFarland. The Heat of Solution of Metals, L. L. Burgess.
Pittsburgh Section 126
  Notes on Carbon Deposition and Reduction of Iron Ores by Carbon Monoxide, G. D. Chamberlain. Steel Manufacture, F. W. Crabtree. The Analysis of Aluminum and its Ores, E. Blough. The Depression of the Freezing Point by Vinegar, A. Silverman.
Philadelphia Section 127
  A Description of the Water Works of Philadelphia, Giving Particular Attention to the Filtration Feature of the Water Supply, L. Lloyd. Commercial Benzole, J. M. Weiss.
Northeastern Section 127
  Hydrocarbons of the Formula C_8H_{16}, L. Clarke. Artificial Optical Activity, A. W. Ewell.
Louisiana Section 127
  Relation of the Pharmacopoeia to the Chemist, P. Asher. Linseed Oil, G. A. Moffett.
Minnesota Section 127
  Report of the San Francisco Meeting of the American Chemical Society, G. B. Frankforter and C F. Sidener. Report of the Chicago Meeting of the American Electrochemical Society, F. C. Frary. The India Rubber Industry, E. W. McCreery
Chicago Section 128
  The Corpuscular Theory of Matter, R. A. Millikan.
Columbus Section 128
  American Chemical Society Excursion to the California Meeting, A. M. Patterson Measurement of the Temperatures of Electric Furnaces, W. D. Bancroft.
Kansas City Section 129
  The Manufacture of Buttons from Vegetable Ivory, J. P. Trickey. The Whaling Industry, E. R. Weidlein. Some Problems in Animal Nutrition, P. F. Trowbridge.
Nebraska Section 129
  The Magnesia Separation in the Yttrium Group Earths, B. Dales.
Cincinnati Section 129
Georgia Section 129
  The Use of Silver Phosphate as a Standard and a Critical Study of the Gravimetric Magnesia Method for Phosphoric Acid, W. C. Dumas.
Michigan Section 130
Section of Western New York 130
  Cryolite and its Industrial Applications, A. S. Halland.
Indiana Section 130
  Preventive Medicine and the Extremes of Life, C. S. Woods. Color Methods in Iron and Steel Works Practice, H. A. Schwartz.
Wisconsin Section 130
  The Present State of the Tivalency of Carbon, M. Gomberg.
Washington Section 130
Section of Eastern New York 130
  Water Filtration and Hypochlorite Treatment, G. E. Wilcomb. Chemistry of Road Building, W. C. Chalker.
Deceased Members 131

Proceedings.

COUNCIL.

MEMBERS ELECTED BETWEEN NOVEMBER 15TH AND DECEMBER 15TH.

Alexander, Clive M., Iowa City, Ia.
Anderson, Edward X., Iowa City, Ia.
Andrews, Joseph C., 119 Stewart Ave., Ithaca, N. Y.
Anthony, Olney P., care Geo. H. Morrill Co., Norwood, Mass.
Armstrong, Eli H., East Point, Ga.
Beebe, Philip S., 127-14th Ave., Columbus, Ohio.
Boies, O. W., 438 Cascadilla Bldg., Ithaca, N. Y.
Briggs, Thos. Roland, 126 Highland Ave , Ithaca, N. Y.
Brown, James, Aledo, Ill.
Bruni, Giuseppe, University of Padua, Padua, Italy.
Bryce, J. R., 119 Dryden Road, Ithaca, N. Y.
Burns, William McG., 74 Batavia St., Boston, Mass.
Calderwood, Howard N., Jr., 1328 Ohio St., Lawrence, Kans
Callaway, R. S., 2114 Tremont St., Minneapolis, Minn.
Clark, Horace H., 208 So. 43rd Ave., Chicago, Ill.
Conley, Albert D., Box 168, Orono, Maine.
Cozzens, L. S., 108 Brooklyn Ave., Freeport, N. Y.
Cross, L. J., 123 Linn St., Ithaca, N. Y.
Crown, H. A., 110 Stewart Ave., Ithaca, N. Y.
Dennery, Raphael, 1821 Milan St., New Orleans, La.
Dover, Miss Mary V., Mount Holyoke College, So. Hadley, Mass.
Englund, Carl, Vermillion, So. Dak.
Evans, J. Clifford, Doughty House, Millville, N. J.
Flint, Edgar M., Hartley Hall, Columbia Univ., New York City.
Flint, Wm. R., Kent Chemical Laby., New Haven, Conn.
Gluck, H. J., 110 Stewart Ave., Ithaca, N. Y.
Harrison, Benjamin H., 304 E. Daniel St., Champaign, Ill.
Hendrick, Ellwood, 139 E. 40th St., New York City.
Hinman, J. J., Jr., 515 E. Eleventh St., Indianapolis, Ind.
Holmes, August, University of Nevada, Reno, Nev.
Houlehan, Arthur E., 804 E. Seneca St., Ithaca, N. Y.
Humphrey, I. W., 1123 Conn. St., Lawrence, Kans.
Hunez, Vasco, 408 Eddy St., Ithaca, N. Y.
Iveson, W. Lawton, McMaster Hall, McMaster Univ., Toronto, Canada.
Janer, José, 155 W. 64th St., New York City.
Jones, R. L., 151-8th Ave., North, Nashville, Tenn.
Kehoe, Forrest W., S. Main St., Great Barrington, Mass.
Kelly, Theodore B., University of California, Berkeley, Calif.
Kelly, William J., Emilien Strasse 34 III, Leipzig, Germany.
Kewley, James, Balik Papan, East Borneo.
Koenig, W. A., 1419 Poplar St., Philadelphia, Penna.
Kribs, Herbert Guy, Zool. Laby., Univ. of Penna., Phila., Pa.
Manson, David, 138th St. and Broadway, New York City.

Mason, A. O., 17 South Ave., Ithaca, N. Y.
Maynard, W. H., Knoxville, Tenn.
McCoy, H. G., 108 Cascadilla Park, Ithaca, N. Y.
Merriam, Cyrus L., Plantation Oaxaquena, Santa Lucrecia, V. C., Mexico.
Millar, James Hill, Chief Chemist's Lab., St. James Gate, Brewery, Dublin, Ire.
Morse, Harry W., Jefferson Physical Lab., Cambridge, Mass.
Myers, J. E., 81 Lancaster St., Albany, N. Y.
Pettit, James H., University of Illinois, Urbana, Ill.
Proctor & Gamble Co., Cincinnati, Ohio.
Ray, W. L., 315 Lake St., Madison, Wis.
Reed, Burleigh B., 329 E. Jefferson St., Iowa City, Ia.
Riegger, Harold E., 109 Cook St., Ithaca, N. Y.
Rosin, Joseph, 1513 South 6th St., Philadelphia, Pa.
Rowell, Miss Jennie L., 411 Main St., Burlington, Vt.
Schmidt, George A. Co., 236 North Ave., Chicago, Ill.
Shackelford, Harvey, Box 252, Columbia, Mo.
Silver, C., 127 College Ave., Ithaca, N. Y.
Smith, Arthur, Jamieson Ave., Collegiate Inst., Toronto, Canada.
Sohn, Erwin, 1852 West 112th St., Cleveland, Ohio.
Sperry, Walter A., 45 S. Harris Ave., Columbus, Ohio.
Stewart, Fred C., 16 Concord St., Portland, Maine.
St. John, Harry M., 118 Ferris Place, Ithaca, N. Y.
Stockton, F. W., Lawrence, Kans.
Sutker, S., 4th and Cherry Sts., Gadsden, Ala.
Tapp, Edward, 2645 Park Ave., Chicago, Ill.
Tingley, Claude S., DeLand, Fla.
Walker, W. F., Mulberry, Fla.
Welch, Harry V., University of California, Berkeley, Calif.
Whipple, LeRoy F., Experiment Station, Kingston, R. I.
Winser, R. A., 207 So. Lincoln Ave., Aurora, Ill.
Wyer, Malcom G., Iowa City, Ia.

BOARD OF DIRECTORS.

The Directors of the American Chemical Society met at the Chemists' Club, New York City, at 3 P.M., Saturday, December 18th, with Messrs. Whitney, Bogert, Hallock, McMurtrie, Parker and Parsons present.

After careful consideration of the estimates by the various officers and the income of the Society, a budget was approved to be presented to the Council at the annual meeting. This budget as finally adopted will be found in the Proceedings of February, 1910.

It was voted that the subscription rate for the Society's publications be as follows:

Any one of the three publications	$ 6.00
Any two of the three publications	10.20
All three publications	12.60

with $16^2/_3\%$ discount to the trade, libraries and clubs of ten or more individuals, and a further discount of fifty cents per subscriber on the combined rates above stated to clubs of twenty-five or more furnished through any firm, corporation, association or individual.

It was voted that these subscription rates shall begin with the March issue of the Journals and that no subscriptions under the old rates shall be accepted to expire later than February 20, 1911.

The meeting then adjourned. CHARLES L. PARSONS, *Secretary.*

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

UNIVERSITY OF MISSOURI SECTION.

The first regular meeting was held on Friday evening, October 1st, at 7 o'clock, in the Chemistry Building. Dr. P. F. Trowbridge presented a paper on "Sodium Benzoate and the Referee Board."

The second regular meeting was held on Friday evening, October 15th, at 7 o'clock, in the Chemistry Building. Mr. P. K. Francis addressed the Section on "The Detroit Meeting of the American Chemical Society."

The third regular meeting was held on Friday evening, October 29th, at 7 o'clock, in the Chemistry Building. Dr. Hermann Schlundt presented a paper on "The Winnipeg Meeting of the British Association for the Advancement of Science."

The fourth regular meeting was held Friday evening, November 19th, at 7 o'clock, in the Chemistry Building. The paper of the evening was presented by Dr. P. F. Trowbridge on "Factors which Influence the Digestibility of Feed."

The fifth regular meeting was held Friday evening, December 3rd, at 7 o'clock. R. C. Palmer spoke on "Explosive Antimony." R. B. Gibson reviewed the "Synthesis of Pyrimidine."

C. ROBERT MOULTON, *Secretary.*

INDIANA SECTION.

The Section met October 8th at Shortridge High School, Indianapolis.

Annual reports from the officers were read. The following were elected for the ensuing year: *President*, R. B. Moore; *Vice-President*, P. N. Evans; *Secretary-Treasurer*, A. D. Thorburn; *Executive Committee*, John White, R. P. Noble, H. E. Bishop. President R. B. Moore addressed the Section on "The Relation of Radioactivity to the Other Sciences."

The Section met Friday evening, November 12th, in the office of the State Food and Drug Laboratory.

The following papers were presented:

"A Study of the Preparation and Preservation of Crushed Fruit and Fruit Syrups," by Ivy L. Miller. "Some Analyses of Tomato Catsup," by H. E. Bishop. (*a*) "Temperance Beers." (*b*) "Estimation of

Dextrose, Dextrin and Maltose," by H. E. Barnard. About 20 members were present.
A. D. THORBURN, *Secretary.*

CHICAGO SECTION.

The November meeting was held at Kent Chemical Laboratory, University of Chicago, on Friday evening, November 12th, at 8.00 o'clock.

The lecture of the evening was on "The Electric Theory of Oxidation and Reduction," by Prof. Julius Stieglitz, University of Chicago.

The University laboratory was open for inspection during the evening.

Seventy-eight attended dinner at 6.15 P.M. and 200 were present at the meeting which was perhaps the best the Chicago Section has ever held.

A. L. NEHLS, *Secretary.*

UNIVERSITY OF ILLINOIS SECTION.

The November meeting was held November 16th, at the Chemistry Building.

The following papers were presented: "The Determination of Nitrogen by the Kober Method," by F. W. Gill. (1) "The Relation of the Water Supplies to the Typhoid Fever Death Rate in Illinois." (2) "A New Thermo-regulator for Incubators," by Dr. E. Bartow.

L. H. SMITH, *Secretary.*

PHILADELPHIA SECTION.

The regular meeting of the Section was held at the Engineers' Club, Philadelphia, Thursday evening, November 18th, at 8 o'clock.

The following three Councilors were elected for 1910: G. E. Barton, D. W. Horn and W. T. Taggart.

The program was: Legal Aspects of Chemistry—symposium. "The Work of the Expert Witness," by Samuel P. Sadtler. "Textile Problems and Disputes," by Frederic Dannerth. "The Legal Side of Toxicology," by Matthew Beardwood. "The Enforcement of the Food and Drugs Act," by C. S. Brinton.

The usual informal dinner was served at 6.30 P.M.

The regular December meeting was held at the Engineers' Club, Philadelphia, Thursday evening, December 16th, at 8 o'clock.

After the usual dinner the following program was presented: "The Purification of Water by Ozone with Remarks on the Commercial Production of Distilled Water," by Henry Leffmann, illustrated by apparatus and lantern slides. "The Jedun Vacuum Evaporator and Its Application to By-products," by A. P. Smith, illustrated by lantern slides. "Mondia Milk," by A. E. Kitson.
F. E. DODGE, *Secretary.*

LOUISIANA SECTION.

The thirty-fifth regular meeting was held on Friday, November 19th, at 8 P.M., in the Directors' Room of the New Orleans Board of Trade. President F. C. Johnson presided and the attendance was very good.

The program for the evening consisted of a paper by Mr. W. J. McGee on the "Manufacture of White Lead from Galena." Mr. McGee spoke of a new process using the lead ore directly as a starting material and carried the process through its various chemical and financial aspects. Later he spoke of the adulteration of white lead with barytes. A general discussion followed the reading of the paper and a vote of thanks from the Society was tendered Mr. McGee. W. L. HOWELL, *Secretary.*

SECTION OF WESTERN NEW YORK.

The regular meeting was held November 19th, Vice-President Lidbury presiding.

The program was of a general nature, several members making reports on special subjects as follows: "Estimation of Small Quantities of Arsenic, by Sanger's Modification of the Gutzeit Test," by W. H. Watkins. "The Action of Bacteria on Minerals," by Geo. Morgan. "Color in Preserved Fruits after Treatment with Lead Subacetate," and "New Sanitary Regulations in Raising and Shipping Oysters," by W. L. Dubois. "Microphotographs of Fine Points and Fibers," by Mr. Morey. "Errors in the Analysis of Linseed Oils," by G. H. Pickard. "Some Delicate Pycnometers and Glass Pens," by R. E. Fowler. "Vanadium in Chrome Iron Ore," and "Periodic Phenomena in the Aluminum Electrolytic Rectifier," by Ross Phillips. N. W. SHED, *Secretary.*

NEBRASKA SECTION.

The fifty-seventh annual meeting of the Section was held in the Lecture Room of the Chemistry Laboratory of the University of Nebraska, Saturday, November 20th, at 8 P.M., with the following program: "Universities I Have Visited," by Chancellor S. Avery. "The Reaction of the Blood," by Dr. C. F. Crowley. "Studies in Asphalt," by Mr. C. J. Frankforter.

The fifty-eighth annual meeting of the Section was held in the Lecture Room of the Chemistry Laboratory of the University of Nebraska, Wednesday, December 15th, at 8 P.M.

The Section listened to addresses on "Some Notes on the Meeting of the British Association," by Dr. F. J. Alway, and on "Systematic Separation and Detection of the Common Acids," by Mr. O. L. Barnebey.

BENTON DALES, *Secretary.*

CORNELL SECTION.

The November meeting was held Tuesday evening, November 23rd, at 8 o'clock. In order that illustrative experiments might be shown, the Section met in Rockefeller Hall. The lecture was by Prof. J. S. Shearer on "The Measurement of High Temperatures by Various Pyrometers." L. M. Dennis was re-elected Councilor for the coming year. Light refreshments were served after the meeting.

The December meeting was held in Morse Hall, Wednesday, December 15th, at 8 P.M. Prof. H. N. Ogden presented the subject: "Disposal of Sewage." A light lunch followed the meeting.

H. W. GILLETT, *Secretary*.

NORTHEASTERN SECTION.

The ninety-fifth regular meeting of the Section was held Friday, November 26th, at 8 P.M., at the Twentieth Century Club, Boston.

Doctor P. A. Levene addressed the Section upon "The Bio-chemistry of Nucleic Acid."

Professor H. A. Torrey, of Harvard University, followed with an address upon "Alkali-insoluble Phenols."

The election of officers and members of the Council for 1910 results as follows: *President*, S. W. Wilder; *Vice-President*, Karl Langenbeck; *Secretary*, K. L. Mark; *Treasurer*, H. C. Lythgoe; *Executive Committee*, F. E. Gallagher, W. C. Bray, G. S. Forbes, G. R. Underwood, L. C. Newell; *Councilors*, L. P. Kinnicutt, G. N. Lewis, W. L. Jennings, H. J. Skinner Dinner was served at 6.30 P.M.

KENNETH L. MARK, *Secretary*.

KANSAS CITY SECTION.

The November meeting was held in Kansas City, Kansas, on Saturday evening, November 27th.

The program began at 5.30 P.M., with a paper by Professor E. H. S. Bailey on the "Benzoate of Soda Discussion."

After supper Mr. Ralph E. Shuey read a paper on the "Practical Advantages of Drying Alfalfa by Artificial Heat."

The December meeting was held at the Eldridge Hotel, Lawrence, Kansas, on Saturday evening, December 11th.

The Section met in the parlor of the Hotel at 5 o'clock. Officers for the coming year were announced: *President*, F. W. Bushong; *Vice-President*, M. Brayton Graff; *Secretary-Treasurer*, E. A. White; *Assistant Secretary*, D. F. McFarland; *Councilor*, E. H. S. Bailey.

After a fifteen-minute talk by the President- and Vice-President-elect dinner was served, followed by a lecture on "Some Rare Earth Separation Methods," by Professor Benton Dales, Univ. of Nebr.

E. A. WHITE, *Secretary*.

RHODE ISLAND SECTION.

The second meeting of the Section was held at the University Club, Thursday evening, December 2nd. Dinner was served promptly at 7 o'clock.

Dr. H. J. Wheeler, Director of the Rhode Island Argicultural Experiment Station, then presented the paper for the evening on "The Influence of Sodium and Potassium Salts upon the Subsequent Yield of Potato Tubers Planted under Like Manurial Conditions."

ALBERT W. CLAFLIN, *Secretary*.

MILWAUKEE SECTION.

The regular meeting of the Section was held Friday evening, December 3rd, at the Blatz Hotel. Dinner was served at 6.30 P.M. with 35 present. After a lecture on "High Temperatures and Other Measurements," by Mr. Otto Kowalke, Mr. W. V. Young, of the Hoskins Mfg. Co., of Detroit, gave a practical demonstration of pyrometers and electric furnaces.

H. M. SOPER, *Secretary.*

GEORGIA SECTION.

The December meeting was held at the State Capitol on December 4th, and the following program given:

"Studies in the Sampling of Mixed Fertilizers, Size of Sample to be Taken," by F. B. Porter. "The Early History of the Cement Industry," by C. N. Wiley. "The Honey Locust as a Cattle Food," by C. A. Wells. "A Triumph of Chemistry Over Bacteriology in the Test of Polluted Waters," by H. B. Arbuckle. "An Investigation of the Stain of the Black Walnut on the Fish of Our Streams," by G. P. Shingler.

The following officers were elected for the year 1910: *President,* R. E. Stallings; *Vice-President,* W. C. Dumas; *Secretary,* J. S. Brogdon; *Councilor,* W. P. Heath.

W. C. DUMAS, *Retiring Secretary.*

LOUISVILLE SECTION.

The December meeting was held in Room 700 of the Atherton Building on the 6th. The paper for the evening was given by C. E. Martin on "Fast Colors on Cotton."

F F. HASBROUCK, *Secretary.*

CINCINNATI SECTION.

The 154th regular meeting was held Wednesday, December 8th, at 8 P.M., in the Chemical Lecture Room of the University of Cincinnati. The topic of the evening, "Some Experiments Illustrating Certain Phases of the Electrolytic Dissociation Theory," was presented by Prof. Lauder W. Jones.

The following officers were elected for 1910: *President,* Joseph W. Ellms; *Vice-President,* Archibald Campbell, Otto Dieckmann; *Recording Secretary,* Alfred Smith; *Financial Secretary,* Max H. Goettsch; *Executive Committee,* B. M. Pilhashy, Clarence Bahlmann, Mortimer Bye; *Councilor,* Alfred Springer.

RALPH E. OESPER, *Retiring Secretary.*

WISCONSIN SECTION.

The annual meeting of the Section was held at Madison on Wednesday, December 8th, at 8 P.M., in Room 102 of the Chemistry Building.

The following address was given: "The Industrial Methods of Obtaining Resinous Products from the Southern Yellow Pine," by Dr. L. F. Hawley, Forest Service, U. S. Department of Agriculture.

FRANCIS C. KRAUSKOPF, *Secretary.*

WASHINGTON SECTION.

The 194th meeting was held Thursday, December 9th, at 8 P.M., in George Washington University.

The program was as follows: "Estimation of Glycerine in Meat Preparations," by F. C. Cook. "Enzymes and Their Relation to Soil Fertility," by M. X. Sullivan. "Detection of Colocynth Seed in Powdered Colocynth," by V. K. Chesnut.

W. B. D. Penniman was elected Councilor in place of E. T. Allen, resigned.

J. A. LECLERC, *Secretary.*

LEHIGH VALLEY SECTION.

The regular fall meeting of the Section was held at the Hotel Allen, Allentown, Friday, December 10th, at 8 P.M.

Election of officers resulted as follows: *Chairman,* J. T. Baker; *Secretary,* Geo. C. Beck; *Councilor,* Geo. P. Adamson.

The papers presented were: "The Relation of Economic Products and Geology in the Lehigh Valley," by B. L. Miller, Professor of Geology, Lehigh University. "A Chemist's Slide Rule," by R. K. Meade. "Decomposition Temperature of Some Sulphates," by W. S. Landis.

A number of members and guests met informally for dinner at 7 P.M.

GEO. C. BECK, *Secretary.*

CLEVELAND SECTION.

The first annual and tenth regular meeting was held in the Geology Department of Case School of Applied Science, December 13th, at 8 o'clock.

The following papers were presented: "The Commercial Manufacture of Oxygen," by Charles F. Brush. "The Brick Industry in Cleveland," by Professor F. R. Van Horn, illustrated with lantern slides.

NORMAN A. DUBOIS, *Secretary.*

MINNESOTA LOCAL SECTION.

The 22nd regular meeting was held Friday evening, December 17th, in the Chemical Laboratory, University of Minnesota.

The papers presented were: "The Reaction between Ammonium Chloride and Potassium Dichromate when Heated," by G. B. Frankforter, V. H. Roehrich and E. V. Manuel. "The Nucleation of Mixed Vapors in Dust-free Air," by I. H. Derby and E. X. Anderson.

FRANCIS C. FRARY, *Secretary.*

DECEASED MEMBERS.

Irving E. Beach, Lawrence, Mass.
Edward M. Davies, November 24th, Saltville, Va.
Irwin La Verne Powers, August 28th, Niagara Falls, N. Y.
Arthur McBride Ransom, Auburn, Ala.
Edward C. Smith, September 17th, Joliet, Ill.
Herbert H. Wing, Monticello, N. Y.
John A. Young, November 10th, San Francisco, Calif.

Issued with the February Number, 1910.

Proceedings.

MINUTES OF THE FORTY-FIRST GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The forty-first general meeting of the American Chemical Society was held in Boston, Mass. in affiliation with the American Association for the Advancement of Science, from Tuesday, December 28, to Friday, December 31, 1909.

The meeting opened with meetings of the Industrial, Organic and Physical and Inorganic Divisions and the Section of Chemical Education on Tuesday in the Lowell Building of the Massachusetts Institute of Technology. Dr. D. L. Randall acted as press secretary for *Science*.

The program and abstracts of the minutes of the various Divisions and Sections are given later in these pages.

On Tuesday afternoon excursions were enjoyed to chemical works and on Tuesday evening a "smoker" complimentary to the visiting chemists was given by the Northeastern Section at the Hotel Brunswick, where an extremely interesting program containing many humorous events was enjoyed.

On Wednesday the Society met in general meeting in the New Lecture Hall of Harvard University and the following addresses were presented in general session.

Methods Employed in Precise Chemical Investigations. T. W. Richards.

On the Constitution of Curcumine—the Coloring Matter of Turmeric. C. Loring Jackson and Latham Clarke.

The Application of Physical Chemistry to the Study of Oleoresins. Charles H. Herty.

The Function of Chemistry in College Education. Lyman C. Newell.

The Cause of Color in Organic Compounds. Richard S. Curtiss.

The United States Pharmacopoeia and the American Chemical Society. Joseph P. Remington.

The Past and Future of the Study of Solutions. Louis Kahlenberg, retiring Vice-President Section C, American Association for the Advancement of Science.

The Chemist's Place in Industry. A. D. Little.

In the evening President Whitney's address was delivered before the assembled chemists in the Lowell Building of the Massachusetts Institute of Technology and was upon the subject: "Some Chemistry of Artificial Light." The lecture was experimentally illustrated.

On Thursday morning a general business meeting of the Society was held in the Lowell Building at which the reports of the officers of the Society were received and read. The following miscellaneous business was then transacted.

It was reported to the members that a majority of the Council had approved the nomination of the Right Honorable John Wm. Strutt (Lord Rayleigh), Madame S. Curie, Professor J. D. van der Waals, Sir James Dewar, Professor R. Fittig and Professor J. W. Mallet for honorary membership in the Society and that all preliminaries required by the Constitution for their election had been met. On motion from the floor, each of the before-mentioned chemists was unanimously elected to honorary membership in the Society.

Dr. H. P. Talbot presented the same resolutions which were passed by the Council in memoriam of Charles Benjamin Dudley and these were unanimously adopted by the Society by rising vote. They will be found in full in the Proceedings of the Council.

Mr. S. T. Mather spoke for a few moments to the meeting in regard to the summer meeting in San Francisco and the many pleasures awaiting the members there and invited the Society to examine the borax mines of the Thorkildsen-Mather Co. at Lang, California, near which it was anticipated the train carrying the members might pass.

The attention of the Society was called to the Berthelot Memorial being erected to one of our deceased honorary members and the desirability that members of the Society should contribute thereto. It is hoped that further subscriptions of one or two dollars each may be received by the Secretary, which will be duly acknowledged.

The President then announced the election of Wilder D. Bancroft as President of the Society and Alexander Smith, A. D. Little, L. H. Baekeland and W. L. Dudley as Councilors-at-Large.

Following this announcement a unanimous vote of thanks was passed to the President and chemical faculty of the Massachusetts Institute of Technology and to the President and chemical faculty of Harvard College for the courtesies extended to the Society and for the use of their buildings and lecture halls; to A. D. Little, T. W. Richards, A. A. Noyes, W. H. Walker, C. R. Sanger, H. P. Talbot, J. F. Norris and H. A. Torrey, Chairman of the local committees, and to the members of those committees for their unceasing efforts in our behalf, and to Walter Baker Chocolate Co., New England Gas & Coke Co., Massachusetts Breweries Co., Wood Worsted Mills, Forbes Lithograph Mfg. Co., American Woolen Co., Champion International Co., Felton & Sons, Inc., Fore River Ship-Building Co. and the Massachusetts State Board of Health for the privileges accorded to our members to examine their various works and laboratories.

The business meeting then adjourned and the Society met in divisional and sectional meetings throughout Thursday and Friday in the Lowell Building.

On Thursday night at 7 o'clock the annual subscription dinner was held in the banquet hall of the Somerset Hotel and was very largely attended and thoroughly enjoyed by all.

On Friday afternoon excursions were participated in by the members to Lawrence, Mass., where the Wood Worsted Mills, the Water Supply and Sewage Experiment Station of the State Board of Health and the Water Filtration Plant were examined; to Fore River, where the Fore River Ship-Building Co. was visited, and to South Boston to visit the distilleries of Felton & Son, Inc.

The meeting was the largest ever held by the American Chemical Society and the continually increasing enthusiasm prevalent throughout the Society was everywhere manifest. 558 members and guests registered and a considerable number were present whose names were not secured. The number of guests approximated 30.

The papers read before the meeting will be found under the divisional heads which follow later.

Report of the Secretary for 1909.

The current year has been no exception to the continued progress of the American Chemical Society and there was never a time in its history when the chemists of the country were more thoroughly organized and in hearty accord and sympathy with the work which it is trying to do. The publications have been issued promptly throughout the year with the single exception of the December number of the *Journal of Industrial and Engineering Chemistry*, which was held up on account of difficulties with the Index. The policy of organizing the Society in Divisions, begun in 1908, has been continued during the year and the Divisions of Physical and Inorganic Chemistry, Fertilizer Chemistry, Agricultural and Food Chemistry, Organic Chemistry and Pharmaceutical Chemistry have been organized and their work is daily growing in importance. The Baltimore Meeting was the largest ever held in the history of the Society and the Detroit Summer Meeting, while smaller in numbers than the Winter, which is always the case, had the largest attendance of any meeting ever held by the Society in the summer time.

During the year the Society has passed the record of all other chemical societies in regard to the numbers of its membership and is now the largest chemical society in the world. The membership of the Society at the time of the Baltimore Meeting was 4004. It is now 4502, a net gain of approximately 500 members. The membership statistics are as follows:

Honorary members	12
Life members	13
Corporation members	17
Members	4460
Total	4502
Elected during 1909 but not yet qualified	62
Grand total	4564

During the year the Society has lost by death one of its honorary members, Julius Thomsen, of Copenhagen, Denmark, and the following members: Gilbert N. Batchelder, Manzanillo, Cuba; Irving E. Beach, Lawrence, Mass.; John D. Billings, Syracuse, N. Y.; Edward M. Davies, Saltville, Va.; H. Augustus Hunicke, St. Louis, Mo.; John P. Ihart, Liberty, N. Y.; William Lyon, Los Angeles, Calif.; John K. Mackenzie, Chicago, Ill.; S. E. Nelson, Devil's Slide, Utah; Irwin La V. Powers, Boston, Mass.; Arthur McB. Ransom, Auburn, Ala.; Edward C. Smith, Joliet, Ill.; C. E. Strunz, Pueblo, Colo.; A. Sydney Warren, Buffalo, N. Y.; A. F. Watson, Dublin, Ireland; W. F. Wheeler, Urbana, Ill.; Herbert H. Wing, Monticello, N. Y.; Theodore R. Wolf, Newark, Del.; Heman A. Wood, Fargo, N. D.; John A. Young, San Francisco, Calif.; C. Irving Zimmerman, Madison, Wis.

The number of members not in arrears registered in the Local Sections on December 1, 1908 was 2816, and on December 1, 1909 was 3237.

The numbers in each Section for 1908 will be found in the Proceedings of 1909, page 17. For 1909 they are as noted below.

During the year the Local Sections have, as heretofore, shown strong loyalty to the welfare of the whole Society and have fully met the spirit which pervades almost all of the Sections of due economy in their local expenses in order that the funds of the Society may be utilized to meet the great cost of our publications, as most of the members realize fully that the Society is expending a much larger proportion of its income upon its publications than any other unendowed society in the world. Every member secures the benefit of any sacrifice he may make in his Local Section by the increased good which results to the whole Society therefrom.

According to the change in the Constitution the accounts with the Local Sections were placed in the hands of the Secretary to whom their treasurers make report. The following is a summary of the sectional accounts for the year, showing the number of members in each, the balance of funds saved by them in 1908 and credited to their 1909 account and the amounts drawn from the Treasurer's office in 1909; also the expense per member in each Section.

American Chemical Society 1909 Account with

Local Section.	No. paid members.	Cr.	Dr.	Expense per member.
California	148	9.88	109.88	0.74
Chicago	250	122.19	172.19	0.69
Cincinnati	77	00.00	115.50	1.50
Cleveland	109	00.00	40.00	0.36
Columbus	45	49.80	49.80	1.10
Cornell	27	50.90	24.90	0.90
Eastern New York	50	00.00	50.00	1.00
Georgia	27	00.00	15.00	0.55

AMERICAN CHEMICAL SOCIETY 1909 ACCOUNT WITH

Local Section.	No. paid members.	Cr.	Dr.	Expense per member.
Indiana	58	13.25	73.25	1.26
Iowa	38	00.00	7.70	0.20
Lehigh Valley	41	0.63	25.63	0.62
Louisiana	27	00.00	25.00	0.93
Louisville	22	00.00	20.00	0.91
Kansas City	80	00.00	80 00	1.00
Michigan	107	73.25	73.25	0.68
Milwaukee	42	00.00	61.50	1.50
Minnesota	56	0.80	25.80	0.37
Nebraska	24	10.61	10.61	0.44
New York	666	00.00	100 00	0.15
North Carolina	26	00.00	30.00	1.15
Northeastern	382	13 03	313.03	0.82
Philadelphia	217	00.00	200 00	0 92
Pittsburg	145	42.57	142.57	0.98
Puget Sound	30	00.00	25.00	0 83
St. Louis	63	29.13	89.13	1.41
Syracuse	61	00.00	50.00	0.82
Washington	229	00.00	150.00	0 66
Western New York	65	00.00	97.50	1 50
Wisconsin	51	18.51	68.51	0.98
University of Illinois	54	14.81	39 81	0.74
University of Missouri	20	00 00	10.00	0.50
	3237	449.36	2295.56	0.61

It is worthy of note that in spite of the increased membership of the Local Sections during the year there has been a slight decrease in cost per member.

During the fiscal year, December 1, 1908, to December 1, 1909, the Secretary has made collections to the amount of $48,969.12, divided as follows:

Members' subscriptions	$41,763.50
Subscriptions from non-members	2,979 38
Sales of back numbers	3,100.84
Foreign postage	515.29
Reprints	369.90
Reinstatements	52.55
Exchange	11.93
Interest	175.73

This amount was duly transmitted to the Treasurer of the Society.

The special sale of back numbers, which was begun in 1908, was continued by vote of the Directors until April 1, 1909. The effect of this sale has been noteworthy, as a distinct interest was aroused throughout the country and throughout the world to fill up partial sets and partial volumes so that the back number account, the receipts of which were estimated at $500.00 for the year, really assumed the magnitude of $3,100.84. On the close of the sale several thousand copies of certain excessive issues of copies of the *Journal of the American Chemical Society* were destroyed, leaving the stock in much better condition than before, and by purchase of certain months that were nearing exhaustion the stock is still as a whole in excellent condition. The Journals which in the early part of the year were stored in a basement near the office of the Eschenbach Printing Company, have been removed to the new building erected by them without expense to the Society and are now in excellent condition.

The following is a summary of the back numbers sent out by the Secretary during the year together with the present stock of journals and the condition of the mailing lists.

Copies of the Society's publications sent out from December 1, 1908, to December 1, 1909, aside from the mailing lists	31,724
Copies of the Journals and Chemical Abstracts in stock	44,068
Copies of the General Index in stock	495
Copies of the Anniversary Number in stock	298
Mailing list for both Journals and Abstracts	4,187
Mailing list for Abstracts only	157
Mailing list for Journal only	412
Mailing list for Industrial Journal only	104

It is still desired to purchase certain back copies of the Journal and members will confer a favor upon the Secretary by looking through their stock and comparing it with the advertising pages of the *Journal of the American Chemical Society*, where a regular advertisement is run by the Secretary with offers for missing back numbers. Vols. 3, 4, 5, 17, 18, 20 and 22 have already been reduced below the limit set by the Council for their sale except in complete sets. The Society now has but three complete sets of its publications left for sale.

Perfect harmony exists throughout the whole Society and all of our members appear to be working together with decided enthusiasm for the upbuilding of American chemistry and the circulation of the results of American chemical research.

The Secretary wishes to take this opportunity to thank the members throughout the Society for the loyal support which they have given him in his efforts to increase our strength and usefulness throughout the country. Early in the year he sent a communication asking for their support in the attempt to bring up the membership of the Society to 4500 and the loyalty and enthusiasm with which they responded is shown by the fact that this number was not only reached but exceeded.

CHARLES L. PARSONS,
Secretary.

Report of the Editor of the Journal of the American Chemical Society and Chemical Abstracts.

During the year ending November 30, 1909, 179 papers have been submitted to the Board of Editors of the *Journal of the American Chemical Society*. Of these 147 have been or will be published, 11 have been published after revision by the authors, and 21 have been returned for revision, or because they were not suitable for publication in the Journal. The number of pages printed during the last three years is as follows:

	1907	1908.	1909.
Proceedings	92	130	116
Original papers	1624	1736	1271
Reviews	73	110	64
Book reviews	73	77	31

The decrease in the number of pages published is, of course, chiefly due to the fact that papers and book reviews pertaining to industrial chemistry have been published in the *Journal of Industrial and Engineering Chemistry* during the current year. The circulation of the *Journal of the American Chemical Society* for December was 4601 copies, an increase of 628 above the circulation of December, 1908. The edition of the January number for 1910 will be 5700 copies.

Owing to the necessity for careful economy we have been compelled to consider very carefully, with regard to all papers submitted, both whether they represent important scientific work which will be of value to our readers and which is worthy of publication in our Journal, and also whether it is possible to present the material offered in a more concise form. I wish to express for the Board of Editors our appreciation of the very kind way in which our criticisms in both directions have been met, and for the assistance which has been given us by our contributors toward securing the publication of all desirable material, without exceeding the sum which was appropriated for the publication of the Journals.

At the beginning of the current year the extended table of contents in *Chemical Abstracts* was discontinued, chiefly from motives of economy, and because it was thought wise to expend the money in other directions. For the same reason the abstracts published during the year have been more carefully examined for the purpose of eliminating those which were of greater length than our funds will permit. The result has been rather an increase in the uniformity of character of the abstracts than any further shortening of those abstracts which were already in a very concise form. It has been possible as a result to publish a larger number of abstracts without increasing the number of pages. The system of checking our abstracts against those published in other abstract journals, and also to avoid duplicate publication, has been further improved, and we think it fair to say that the whole field of chemical publications in the world is more completely covered by *Chemical Abstracts* than by any other similar publication. This will be apparent from the number of abstracts published during the current year, which is as follows:

	1907.		1908.		1909.	
	No. of pages.	No. of abstracts.	No. of pages.	No. of abstracts.	No of pages.	No. of abstracts.
Apparatus	31.8	100	57.2	265	42.7	267
General and Physical Chemistry	162.6	529	268.3	1013	254.1	1081
Radioactivity	26.9	99	55.3	228	34.2	163
Electrochemistry	44.3	132	77.4	240	73.0	312
Photography	12.0	43	29.9	139	14.1	77
Inorganic Chemistry	138.8	426	112.0	412	85.6	371
Analytical Chemistry	61.9	188	208.7	488	108.4	439
Mineralogical and Geological Chemistry	157.6	561	149.9	807	80.5	528
Metallurgy	89.2	320	120.8	490	69.1	315
Organic Chemistry	659.1	1449	630.4	1692	535.1	1475
Biological Chemistry	300.7	1540	213.3	1001	363.5	2120
Foods	122.2	385	136.3	565	148.9	574
Nutrition	39.4	163	39.7	172	48.9	250
Water, Sewage and Sanitation	54.8	190	56.9	202	36.2	127
Soils and Fertilizers	52.1	235	44.3	198	47.8	297
Fermented and Distilled Liquors	29.3	101	41.8	162	42.9	206
Pharmaceutical Chemistry	85.5	316	92.4	503	110.5	674
Acids, Alkalies and Salts	61.9	126	46.1	173	31.8	203
Glass and Ceramics	26.1	66	53.2	185	39.7	217
Cement, Mortar and Building Materials	59.7	94	90.3	378	44.7	175
Fuels, Gas and Coke	78.7	196	58.8	232	74.1	347
Petroleum, Asphalt and Wood Products	21.4	72	27.1	97	35.3	150
Cellulose and Paper	27.9	83	41.7	195	13.5	74
Explosives	25.2	44	42.0	121	50.4	235
Dyes and Textile Chemistry	54.6	105	68.0	192	19.2	79
Pigments, Resins, Varnishes, India Rubber	31.2	95	25.3	86	20.3	92
Fats, Fatty Oils and Soaps	38.6	78	62.1	158	49.8	187
Sugar, Starch and Gums	56.9	186	58.8	207	68.7	350
Leather and Glue	34.0	53	20.5	34	22.3	70
Patents	462.1	...	355.3	..	365.8	3806[1]
	3,046.5	7,975	3,283.8	10,835	2,931.1	11,455

W. A. NOYES, *Editor*.

---

[1] Not included in the total.

Report of the Journal of Industrial and Engineering Chemistry for the Year 1909.

The *Journal of Industrial and Engineering Chemistry* has completed its first year and has published twenty-four editorials, one hundred sixty-eight original papers, or a total of one hundred and ninety-two articles all told. There are on hand at the present time sixteen unpublished articles and during the year there have been rejected twenty-eight articles, making a total number of articles received during the year of two hundred and forty-four.

The articles published have been distributed in the various fields as follows: Chemical Engineering, four; Heavy Chemicals, eleven; Fuels, nine; Glass, none; Metals in general, two; Iron and Steel, nine; Metallurgy of Gold, Silver, Copper, one; Metallurgy of Lead, Zinc, etc., three; Fertilizers, eleven; Pharmaceutical, Essential Oils, etc., eight; Explosives, two; India Rubber, four; Sugar and Starch, five; Water, Sewage and Sanitary Chemistry, three; Foods, thirty; Ceramics, one; Paper, none; Paints and Varnish, Resins, three; Cement, Lime, Plaster, three; Textiles and Dyeing, none; Destructive Distillation and Petroleum, six; Asphalt, Tar, Pitch, etc., four; Oils and Fats, Soaps, Lubrication, nine; Brewing and Spirituous Liquors, one; Gas and Illumination, two; Electro Chemistry, three; Analytical and Apparatus, thirty-four; Soils and Agricultural, ten; Chemical Education, three; Miscellaneous, twelve.

The monthly edition has varied from 5200 to 4600 copies. Some of the issues are now nearly exhausted.

There are increasing evidences that the Journal is finding favor abroad, particularly in England and in France.

It may be well to recall at this time the various steps which led to the establishment of the *Journal of Industrial and Engineering Chemistry* and of the separate features of the Journal. Following an agitation on the part of the industrial chemists belonging to the Society, for more representation in the affairs of the Society and for more published matter devoted to their interests, the idea of an "Industrial Journal" was first seriously discussed in the summer of 1907 at the Toronto meeting. At that meeting a committee was appointed to consider the matter in all its details and to report at the Chicago meeting, in the winter of 1907–1908. This committee, after correspondence and discussion in meetings, agreed upon the general plan of the *Journal of Industrial and Engineering Chemistry* as it exists to-day, and the Council, after a full and open discussion, adopted the report at the Chicago meeting. Appropriations for the Journal were passed at the Baltimore meeting in the winter of 1908–1909. Each department which has been established in the *Journal of Industrial and Engineering Chemistry* was established by unanimous vote of the committee which had the original plans in charge and by unanimous vote of the Council after a full discussion. It should be remembered that there were good reasons for establishing each department of the Journal or it would not have been established. There are equally good reasons for continuing the department until it is shown to be without value to a considerable number of our membership.

A scientific society which undertakes to publish journals for its members, it is not in the position of a private person or corporation, which publishes papers in the interests of a more or less narrow group of readers and in the interests of his advertisers. A scientific monthly published by a society is usually an outgrowth of the publication of the proceedings of the annual or semi-annual meeting; that is, in the early days of many scientific societies, when the number of members is rather limited, the society's funds will only permit the publication of an annual or semi-annual volume of proceedings which includes papers and sometimes discussions presented at those meetings. As the society grows, to facilitate prompt publication, a monthly may be established to take the place of the earlier proceedings. And such a publication, no less than the proceedings, is bound to publish all worthy research papers submitted. In considering what constitutes suitable material for publication, consideration must be had of several points. In the first place, a society in entering the publication field, particularly with a monthly journal, has several duties to perform. It is the paramount duty of such a society to publish suitable research material which its members present for publication. This duty of a society, if it publishes at all, must not be overlooked or underestimated, for any reason or consideration whatsoever. This is the essential point wherein a society publication differs from a private one. In the second place, in the case of a journal like the *Journal of Industrial and Engineering Chemistry*, the Society owes a second duty to its members, in the way of publishing material for the better information of its members, which is mainly of temporary interest. Such material may be in the field of engineering chemistry, of the nature of book reviews, new book lists, lists of new patents, industrial and trade notes, discussion and correspondence, or merely personal notes. In the third place, a society in entering the field of publication, owes a duty to the scientific world at large, which consists in publishing the original research papers of its members, which may have little immediate value but which must go on record and so become available for the future scientific public.

It is interesting to note that each man who is interested in a particular subject, regrets that more papers on his subject are not published. This tendency is as natural as it is regrettable. What we should desire is a well-rounded Journal with some papers during the year on each branch of the subject which it endeavors to cover.

Recently a large number of letters were sent out to authors of papers published in the *Journal of Industrial and Engineering Chemistry* during the year, asking for their views on various features of the Journal. Some new suggestions were offered which will unquestionably prove of future benefit, and some criticisms were made, but it is interesting to note that the consensus of opinion as expressed in these letters was decidedly in favor of the *Journal of Industrial and Engineering Chemistry,* as it stands at the present time, inclusive of all its established features. Probably no higher tribunal could judge of the matter than this, unless it should be the whole body of the Society, which is obviously impossible.

The principal necessity which the year has developed is to separate the papers on agricultural and food chemistry from the *Journal of Industrial and Engineering Chemistry* and publish them in a *Journal of Agricultural and Food Chemistry.* Following this, to publish more papers of an engineering chemical nature in the *Journal of Industrial and Engineering Chemistry.* This is an excellent policy. Both Journals would be eminently successful. It would mean a better classification of other material and it would mean that more and better papers on industrial and engineering chemistry would be produced and published. Practically all the material during the past year has come without solicitation. This was necessary because of the fact that funds appropriated for the *Journal of Industrial and Engineering Chemistry* for the year were insufficient to publish all material received. With the successful growth of the Society if we practice economy, we are assured of sufficient funds in the future for all our reasonable undertakings. We can therefore solicit good papers from known authorities on various subjects in the field of engineering chemistry. Your editor has no doubt that a large number of such papers could be obtained, and with such papers available for publication, assurance could be given of a far more useful Journal than has been published up to the present time. In conclusion, it appears that the *Journal of Industrial and Engineering Chemistry* has been founded on sound principles; that it rests upon a firm foundation financially, is demonstrated by the present year's experience, and that with reasonable support it can continue to be most useful to our membership, supplementing our other publications in its particular field. W. D. RICHARDSON.

Treasurer's Report.

Nov. 30, 1908–Nov. 30, 1909.

RECEIPTS.

Balance on hand December 1, 1908		$ 4,766.18
Secretary's office	$48,969.12	
Back numbers and reprints	8.76	
Advertising	6,551.15	
	$55,529.03	

Interest on bank balances:		
Knickerbocker Trust Co.	135.06	
Farmers' Loan & Trust Co.	96.56	
Interest on investments:		
Atlas Portland Cement Co. bonds	120.00	
Interest on special funds:		
Special Investment Fund	70.00	
Life Membership Fund	35.00	
		$55,985.65
Cash retained by local sections		323.36
		$61,075.19

DISBURSEMENTS.

Publications, 1909:		
Printing Journal, 12 numbers	$ 6,314.34	
" Chemical Abstracts, 26 numbers	12,750.10	
" reprints, Journal	482.13	
" I. & E. Journal, 11 numbers	5,937.03	
" I. & E. reprints	687.55	
I. & E. clerical	600 00	
I. & E. expense	254.12	
		$27,025.27
Editor's office:		
Editor's salary	$ 650.01	
Assistant Editor's salary	1,244.97	
Clerical help	1,749.49	
Abstractors	4,476.90	
Expense	568.27	
Reviews	30 00	
		$ 8,719.64
President's office		8.00
Secretary's office:		
Expenses	1,318.19	
Clerical help, etc.	1,153.00	
		2,471.19
Librarian	500.00	
Treasurer's office expense	400.00	
		900.00
Commissions:		
Advertising account, 1908	672.85	
Advertising account, 1909	984.29	
Collection account	1,958.76	
		3,615.90
General meetings		638.12
Local Sections, cash paid		1,846.20
cash retained		323.30
Back numbers, storage, etc.	729.37	
Suspense (postage)	2,146.07	
Reprinting	234.00	
Loans returned	5,200.00	
Interest on loans	10.00	
Index	1,731.95	
Incidentals	283.19	

Deposit to life membership fund	35.00	
Salary, E. G. Love to January 1, 1909	250.00	
Special appropriation	207.94	
		10,827.52
Balance: Farmers' Loan & Trust Co.	3,479.86	
Knickerbocker Trust Co. Rec'rs Cer's	1,142.60	
Knickerbocker Trust Co. Reg'r a/c	77 53	
		4,699.99
		$61,075.19

ASSETS.

As of December 1, 1909.

Special investment fund	$ 2,097.50	
Atlas Portland Cement Co., bonds 6 per cent.	2,210.00	
Life Membership fund ($1,000).	1,080.38	
Life Membership fund in Emigrant Savings Bank.	1,697.25	
Balance: Farmers' Loan & Trust Co.	3,479.86	
Knickerbocker Trust Co (Rec'rs Certfs.).	1,142.60	
Knickerbocker Trust Co. regular account.	77.53	
		$11,785.12
Unpaid dues.	4,100.00	
Uncollected subscriptions	53.65	
Back numbers	340.70	
Reprints	64.25	
Unpaid advertising	750.00	
		5,308.60
		$17,093.72

LIABILITIES.

Life Membership Fund	$ 2,777.63
Excess of assets over liabilities	$14,316.09

ALBERT P HALLOCK,
Treasurer.

Report of the Finance Committee of the American Chemical Society for the Year 1909.

Your committee has during the past year examined and passed upon all the bills sent to the Treasurer for payment and has employed the firm of J. Yalden & Co., certified accountants, to audit the books of the Treasurer and their report is submitted herewith. They find that the accounts of the Treasurer have been carefully and accurately kept and they expressed their entire approval of our present system of accounting.

Respectfully submitted,
PARKER C. MCILHINEY,
GEO. C. STONE,
E. G. LOVE.

Report of the Librarian for the Year 1909.

No additions of especial importance have been made to the Library during the past year. Periodicals received in exchange for the Society's publications have, so far as possible, been bound and added to the Library files. At present the Library contains about 6000 volumes and pamphlets.

LIBRARIAN'S ACCOUNT.

RECEIPTS.

Dec. 23, 1908, balance on hand	$ 47.74	
Feb. 20 to Nov. 15, 1909, from A. P. Hallock, Treasurer	500.00	
		$547.74

DISBURSEMENTS.

Dec. 23, 1908 to Dec. 23, 1909:		
Subscriptions	56.60	
Expense	44.26	
Clerical	163.50	
Filling orders, 1908	53.55	
Binding and completing files	216.60	
Balance on hand	13.23	
		$547.74

E. G. Love, *Librarian.*

Division of Industrial Chemists and Chemical Engineers.

The meetings of the Division were held on Tuesday, Thursday and Friday with Chairman A. D. Little presiding. A full account of their proceedings with list of papers will be found in the February number of the *Journal of Industrial and Engineering Chemistry.*

A special feature was the symposium on the Chemistry of Paint, held Thursday morning, which evoked a lively discussion and at which many interesting points were brought forward besides the important papers that were presented.

Committees of unusual importance to industrial chemists and to the chemical trade were appointed and will be found in the full proceedings. These committees consisted of a Committee on Definition of Trade Terms, Clifford Richardson, *Chairman;* Committee on Trade Customs, Henry Howard, *Chairman;* Committee on Official Specifications, Hervey J. Skinner, *Chairman;* Committee on Research Problems, Geo. C. Stone, *Chairman;* Committee on Standard Methods of Technical Analysis, T. J. Parker, *Chairman;* Committee on Descriptive Bibliographies, Clement W. Andrews, *Chairman;* Committee on Publicity, Wm. McMurtrie, *Chairman;* Special Committee to Confer with Manufacturers for the Purpose of Determining at What Prices Elements and Special Compounds Can Be Obtained Provided a Large Market Is Developed for Them, Gellert Alleman, *Chairman.*

The officers elected for the year 1910 are as follows:

Chairman, A. D. Little; *Vice-Chairman,* Geo. C. Stone; *Secretary,* F. Gallagher, 93 Broad St., Boston, Mass.; *Executive Committee,* The officers and W. D. Richardson, *ex-officio* and W. H. Walker, J. O. Handy, A. S. Cushman, C. P. Van Gundy, L. A. Olney.

B. T. BABBITT HYDE, *Retiring Secretary.*

Division of Physical and Inorganic Chemistry.

The Division met on Tuesday, Thursday and Friday, presided over by Chairman C. H. Herty.

At the business session the following officers were elected for 1910: *Chairman,* E. C. Franklin; *Vice-Chairman,* Alexander Smith; *Secretary,* S. L. Bigelow, Ann Arbor, Mich.; *Executive Committee,* Officers *ex-officio* and W. F. Hillebrand, G. A. Hulett, W. L. Miller, T. W. Richards, H. P. Talbot.

The question of forming a Section of Inorganic Chemistry was brought before the meeting and the Executive Committee was instructed to consider the advisability of forming such a Section, to report to the Council at the San Francisco Meeting if possible. To facilitate matters the Chairman appointed a committee to consider the matter and to report to the Executive Committee. This committee consisted of A. W. Browne, W. F. Hillebrand, T. W. Richards, Alexander Smith, H. L. Wells.

The following papers were presented to the Division:

Some Observations on Phosphorescence. W. L. Dudley.

Solarization without Light. W. D. Bancroft.

Electro-Chemical Investigation of Amalgams of Thallium, Indium, Tin, Lead, Zinc and Cadmium. T. W. Richards, J. Hunt Wilson and R. N. Garrod-Thomas.

The Reduction of Zinc by Mercury and the E. M. F. of Zinc Amalgams. J. L. Crenshaw.

Rôle of Water in Minerals. W. F. Hillebrand.

Ammonolysis of Hydrazine Sulphate. A. W. Browne and T. W. B. Welsh.

Quantitative Application of the Theory of Indicators to Volumetric Analysis. experimentally illustrated. Arthur A. Noyes.

Measuring Capillary Ascension in Metal Tubes. S. L. Bigelow.

The Electrolysis of Copper Sulphate Solutions with Intermittent Current. W. Lash Miller.

The Final Results of an Investigation on the Atomic Weights of Lithium and Silver. T. W. Richards and H. H. Willard.

A Revision of the Atomic Weight of Phosphorus. G. P. Baxter and Grinnell Jones.

A Revision of the Atomic Weight of Neodymium. G. P. Baxter and H. C. Chapin.

The Velocity of Saponification of Formic Esters. Julius Stieglitz.

The Influence of Acids and Alkalies upon the Activity of Invertase. C. S. Hudson and H. S. Paine.

Heats of Combustion of Organic Isomers. T. W. Richards and R. H. Jesse, Jr.

Specific Heat and Heat of Neutralization of Aqueous Solutions. T. W. Richards and A. W. Rowe.

The Nature of Attractive Forces. J. E. Mills.

Changes in Volume during Solution of the Alkali Halides. G. P. Baxter.

A Simple Dynamic Method for Determining the Boiling Points and Vapor Pressures of Liquids or Solids with Small Amounts of Material. Alexander Smith and Alan W. C. Menzies.

The Compressibilities of Organic Isomers. T. W. Richards, J. H. Mathews and C. L. Speyers.

The Solubility of Salts in Concentrated Solutions. Arthur E. Hill.

A Method for Determining Vapor Pressures. Alexander Smith and Alan W. C. Menzies.

A Redetermination of Vapor Pressures of Water and Mercury. Alexander Smith and Alan W. C. Menzies.

On the Oxalates of Hydrazine. J. W. Turrentine.

Some New Double Arsenates. Louis J. Curtman.

A Quantitative Study of the Constitution of Calomel Vapor. Alexander Smith and Alan W. C. Menzies.

Wire Silver in Ores and How It Is Formed. C. E. Swett.

The Electrical Deposition of Zinc. Elwood B. Spear.

The Determination of Antimony by the Gutzeit Method. Charles R. Sanger.

Molybdenum and Tungsten. Colin G. Fink.

Caesium Nitrate and the Mass Action Law for Strong Electrolytes. E. W. Washburn and D. A. McInnes.

Cryoscopic-Cryohydric Studies. S. C. Lind.

The Influence of Temperature on the Formation of Water Gas. J. K. Clement and L. H. Adams.

A Method for Determining the Molecular Weights of Dissolved Substances by Measurement of Vapor Pressure. Alan W. C. Menzies.

The Condensation of Water by Electrolytes. F. K. Cameron and W O. Robinson.

The Hydrolysis of Raffinose by Invertase. C. S. Hudson.

A Relation between the Chemical Constitution and the Optical Rotatory Power of the Sugar Lactones. C. S. Hudson.

A Constant Temperature Regulator. Edward Bartow and Frank Bachmann.

A New Method of Separating Chlorine, Bromine and Iodine. Louis Kahlenberg.

The Estimation of Radium Emanation and of Radium in Common Materials. Merle Randall.

The Solubility Relations of Calcium Sulphate at High Temperatures. Arthur C. Melcher, presented by A. A. Noyes.

A New Test Tube Holder. H. Emerson Wetherill.

Notes on the Preparation of Chromyl Compounds. Harry S. Fry.

The Reaction between Bromic and Hydriodic Acid in Concentrated Hydrochloric Acid Solution. D. L. Randall.

On the Velocities of Certain Reactions between Metals and Dissolved Halogens. Ralph G. Van Name and Graham Edgar.

A New Method of Determining the Potentials between Liquids. Gilbert N. Lewis.

Forces at the Boundary between Two Liquids. W. D. Harkins.

Ionization of Salts in Mixtures with a Common Ion. W. C. Bray and F. L. Hunt.

Ionization of Salts in Mixtures with no Common Ion. Miles S. Sherrill.

Chlorsulphonic Acid and Pyrosulphuryl Chloride. Charles R. Sanger.

The Electrical Conductivity of the Alcohols in Liquid Hydrogen Chloride. E. H. Archibald.

Metallic Titanium. Matthew A. Hunter.

The Chief Determining Factor in the Toxicity of the Metal Ions. L. L. Woodruff and H. H. Bunzel.

The Solubility of Gold in Nitric Acid. Frederick P. Dewey.

The Direct Estimation of all Intensities of Hydrogen Ion Concentration by Means of Di-nitro-hydrochinone. Lawrence J Henderson.

The Nitrogen Thermometer from Zinc to Palladium. A. L. Day and R. B. Sosman.

W. D. BANCROFT, *Retiring Secretary.*

Division of Fertilizer Chemistry.

The meeting of the fertilizer chemists was held on Thursday, December 30th, and was presided over by the Chairman, F. B. Carpenter.

The Secretary's report showed 106 members enrolled in the Division.

At the business meeting the following officers were elected for the year 1910: *Chairman,* F. B. Carpenter; *Vice-Chairman,* B. L. Hartwell; *Secretary and Treasurer,* J. E. Breckenridge, Carteret, N. J.; *Executive Committee,* Officers *ex-officio* and F. P. Veitch, H. A. Huston, W. J. Gascoyne, P. Rudnick.

The Chairman's address, entitled "Influence of Chemistry on Agriculture," was presented before the Division. A more detailed account of the meeting with papers read will appear in the February number of the *Journal of Industrial and Engineering Chemistry.*

J. E. BRECKENRIDGE, *Secretary.*

Division of Agricultural and Food Chemistry.

The Division met on Thursday and Friday, presided over by *Chairman* W. D. Bigelow. The officers elected for the year 1910 are: *Chairman,* C. D. Woods; *Vice Chairman,* G. E. Colby, *Secretary,* B. E. Curry, Durham, N. H.; *Executive Committee,* Officers *ex-officio* and E. W. Hilgard, H. W. Wiley, J. P. Street, C. G. Hopkins.

The address of the Chairman, W. D. Bigelow, entitled "The Construction and Installation of a Technical Laboratory," was presented before the Division. In addition to this many papers were presented. Several of these, owing to lack of time and absence of authors, were read by title. The meeting was regarded as an unusually interesting one on account of the wide variety of subjects treated and because of the very full discussion which was entered into by the members in attendance.

Details of the meeting with a list of papers read will appear in the February number of the *Journal of Industrial and Engineering Chemistry.*

F. M. DORSET, *Secretary pro tem.*

Division of Organic Chemistry.

The Division met on Tuesday and Thursday, with Chairman R. S. Curtiss presiding. On Tuesday morning a special program was arranged which was very largely attended by the members of the Society and consisted of the following two papers:

1. Virgil Coblentz. "Synthetic Medicinals: Recent Progress in Relationship between Physiological Action and Structure."

2. Hugo Schweitzer. "Some Recent Advances in the Chemistry of Coal-Tar Colors."

The Chairman's address was presented in general session.

The Secretary reported 174 registered members of the Division.

The following officers were elected for the year 1910: *Chairman*, E. C. Franklin; *Vice-Chairman and Secretary*, R. H. McKee, Orono, Maine; *Executive Committee*, Officers *ex-officio* and H. A. Torrey, J. Stieglitz, J. E. Bucher.

The following motion of general interest was passed:

"The Division of Organic Chemistry of the American Chemical Society recognizes the great usefulness to chemical research, especially organic research, of the plan as now carried out by the Association of American Chemical Research Laboratories[1] and the even great possibilities of the plan suggested for the Chemists' Club of New York City[2] and wishes to express its approval of these plans."

It was further voted:

That the Executive Committee be and hereby is directed to consider this matter and determine if it is desirable that the Division of Organic Chemistry take further action with regard to it.

The following papers were presented to the Division:

The Action of Acetylene on Iodine Trichloride. H. Edmund Wiedemann.

The Condensation of Methylethyl-ketone by Acids and Alkalies. Alfred Hoffman.

4- and 5-Acetamino Acetanthranils and Quinazolines Derived Therefrom. Marston T. Bogert and C. G. Amend.

Ethyl Phenylimino-malonate and Its Reaction. Richard S. Curtiss and F. Grace C. Spencer.

Melting and Boiling Points of Certain Disubstitution Products of Benzene. J. Bishop Tingle.

Phthalamidic Acids Substituted in the Benzene Nucleus. J. Bishop Tingle and S. J. Bates.

The Constitution of Retene and Its Derivatives. John E. Bucher.

Stereoisomeric Chloromido Ketones. Julius Stieglitz.

The Properties of the Hexa-Substitution Products of Ethane. James F. Norris.

Studies in Tautomerism. S. F. Acree.

Furylacetic Ester and Furyl-Pyrazolones. Henry A. Torrey and J. E. Zanetti.

Hydrazones of Certain Oxy-Ketones; Alkali Insoluble Phenols. Henry A. Torrey.

The Preparation of Styrolene Alcohol. Wm. Lloyd Evans and Lou Helen Morgan.

The Basic Properties of Oxygen; Compounds of Dimethylpyrone and the Halogen Hydrides. D. McIntosh.

The Constitution of Ortho-Benzo-Quinone. Wm. McPherson and Howard J. Lucas.

[1] *Science*, 30, 645.

[2] *Ibid.*, 30, 667.

Esterification and Steric Hindrance. M. A. Rosanoff, C. D. Wright and T. F. Power.

The Constitution of the Carboxonium Salts. M. Gomberg and L. H. Cone.

The Constitution of the Carbothionium Salts and of the Acridine Salts. M. Gomberg and L. H. Cone.

Glycogen Content of Beef Flesh. P. F. Trowbridge and C. K. Francis.

The Constitution of Benzene from the Standpoint of the Corpuscular-Atomic Conception of Positive and Negative Valences. Harry Shipley Fry.

The Formation of Cyclopentadiens. William J. Hale.

Some Organic Compounds of Selenium. Howard W. Doughty.

A Measure of Thermodynamic Positivity and Negativity in Water Solution with Reference to Chemical Reactions of Organic Compounds. C. G. Derick.

The Addition Power of Methylethyl-ethylene. Roger F. Brunel.

Equilibrium at High Temperatures between Isobutyl Bromide and Tertiary Butyl Bromide. Roger F. Brunel.

The Iodine Compound of Pinene and the Resin Formed by the Action of Iodine on Pinene. G. B. Frankforter and B. F. P. Brenton.

RALPH H. MCKEE, *Secretary.*

Division of Pharmaceutical Chemistry.

The Division met on Thursday, December 30th, with Chairman A. B. Stevens presiding.

The by-laws were presented and were adopted by the Division. These will, as required by the Constitution, be referred to the Council for approval.

The following officers were elected for the year 1910: *Chairman*, A. B. Stevens; *Vice-Chairman*, J. M. Francis; *Secretary*, B. L. Murray, c/o Merck & Co., University Place, New York City; *Executive Committee*, Officers *ex-officio* and J P. Remington and Edward Kremers.

The following papers were presented:

Scope of Pharmaceutical Chemistry. A. B. Stevens.

Pharmacopoeial Tests for Ammonium Benzoate. A. Seidell and G. A. Menge.

Strychnine Sulphates. A. B. Stevens.

The Botanical Source of the Crude Drug Known as Wild Yam. H. H. Bartlett.

On the Availability of "Idophenine" in the Separation of Acetanilid and Acetphenetidin. W. O. Emery.

Detection of Colocynth Seed in Powdered Colocynth. V. K. Chesnut

"Analytical Notes on Gamboge." Frank O. Taylor.

"On the Melting Point of Aconitine." Frank O. Taylor.

Pancreatin. John P. Street.

The Relation of the Chemist to Proprietary Medicines. W. A. Puckner.

The Purity Rubric and the U. S. P. Tests, with Notes on Quantitative Methods for Certain Pharmacopoeial Compounds. Atherton Seidell and M. I. Wilbert.

Chairman of the Delegates of the American Chemical Society to the Pharmacopoeial Convention presented a report and led a discussion in regard to matters to be brought before that Convention. Geo. D. Rosengarten.

B. L. MURRAY, *Secretary.*

Section of Chemical Education.

The Section of Chemical Education met on Tuesday and Thursday, presided over by Lyman C. Newell, Chairman The Chairman's address, however, was read in general session on Wednesday.

A special feature of the meeting was the discussion of problems relating to secondary school chemistry.

The following resolutions after careful discussion were unanimously passed:

Resolved, That it is the sense of this Section that there is an urgent need for an improvement in the conditions under which chemistry is taught in secondary schools in that

1. The time allotted to the subject in the ordinary curriculum is not sufficient.
2. The chemistry teacher should not teach other subjects requiring laboratory preparation.
3. Provision should be made, by supplying suitable paid help and by allowing the teacher sufficient time each day during school hours, for the preparation of laboratory material.
4. The teacher should be permitted to purchase, subject to suitable supervision of his vouchers, supplies for current consumption, either from petty cash account or from definite appropriation.
5. Text-books should not be used without the approval of chemistry teachers.
6. A double laboratory period should be considered the equivalent of a single formal recitation.

EDWARD ELLERY,
ALBERT L. SMITH,
M. D. SOHON,
Committee.

About 50 were in attendance.

The following papers were presented:

On the Purpose and Method of the Chemistry Course in the Public High School. Frank B. Wade.

Content and Method of a First Course in Chemistry. M. D. Sohon.

Elementary Chemistry in Vocational Education. Lyman G. Smith.

Conditions under which Secondary School Teachers Conduct Their Work. Albert L. Smith.

Conditions and Equipment in Secondary Schools. Charles R. Allen.

The Case against Qualitative Laboratory Experiments. Edward Ellery.

The Desirability of the More Careful Teaching of the Miscibility of Common and Uncommon Reagents. Charles S. Palmer.

Elementary Chemistry Teaching as a Means of Developing the Power of Independent Scientific Reasoning. Arthur A. Blanchard.

The Teaching of Chemistry in Secondary Schools. Mosby G. Perrow.

Educational Value of Chemistry. W. S. Leavenworth.

The First Course in Chemistry for Secondary Schools. M. D. Sohon.

Section of Biological Chemistry.

The Section met on Thursday in the Lowell Building in joint session with the American Society of Biological Chemists.

The following papers were presented:

Industrial Bacteriology as a Field for Bio-Chemical Investigation. Samuel C. Prescott.

Studies upon the Physiological and Chemical Toxicology of the Sap of the Manzanillo Tree. Jose A. Fernandez Benitez.

The Phosphorus of the Flat Turnip. Burt G. Hartwell and Wilhelm B. Quantz.

Concurrent Oxidizing and Reducing Power of Roots. Oswald Schreiner and M. X. Sullivan.

Ratio of Plant Nutrients as Affected by Harmful Soil Compounds. Oswald Schreiner and J. J. Skinner.

Some Points in the Analysis of Proteins. T. B. Osborne.

A Method for the Determination of Amino Nitrogen and Its Applications. Donald D. Van Slyke.

The Anaphylactic Reaction as a Specific Test for Protein. M. J. Rosenau.

The Manganese-bearing Tissues of the Fresh Water Mussels. H. C. Bradley.

The Determination of Arsenic in Animal Tissues. Charles R. Sanger.

The Estimation of Morphine in Cases of Poisoning. Charles R. Sanger.

The Selective Antiseptic Action of Copper Salts. Alfred Springer.

Stagnation *vs.* Circulation in House Air. Ellen H. Richards and Royce W. Gilbert.

The Relation of Typhoid Fever to the Water Supplies of Illinois. Edward Bartow.

Destruction of the Enzym Invertase by Acids and Alkalies. H. S. Paine

The Action of Enzymes on Sugars. C. S. Hudson.

The Cause of Depression Produced by Molasses. J. B. Lindsey.

The Chemical Organization of a Typical Fruit. A. E. Vinson.

Fixing and Staining Tannin in Plant Tissues. A. E. Vinson.

Cornin: a Glucoside Obtained from Cornus Florida. E. R. Miller.

India Rubber Chemistry Section.

The Section met on Thursday, December 30th, under the chairmanship of Mr. Charles C. Goodrich, of New York City. Mr. Frederick J. Maywald, 89 Pine St., New York City, was elected Secretary and the Section requested that these officers act pending the probable organization of a Division. 28 chemists and manufacturers of India rubber were present at the meeting, representing many of the most important rubber corporations, and decided interest was shown in the organization of a Division and in the work that it was hoped might be accomplished. A preliminary organization was effected, which can readily be made permanent whenever divisional government is granted by vote of the Council.

A committee, consisting of Chas. M. Knight, Edw. A. Barrier, Frederick J. Maywald, Milton E. MacDonald, Wm. G. Hills, Sheldon P. Thatcher, W. C. Geer, Mr. Oelschlaeger and Harvey M. Eddy, was appointed to consider the methods of analysis in examination of rubber and rubber compounds.

Much interest was shown in obtaining complete abstracts of all articles on the Chemistry of India Rubber, and a committee, consisting of H. Hughes, Harold van der Linde and M. L. Allard, was appointed to assist the regular abstractors who might be appointed to care for a special section of rubber chemistry in the *Abstracts Journal.*

A committee on membership, consisting of H. M. Eddy, H. van der Linde and Charles Knight, was also appointed.

There was considerable discussion with reference to the question of specifications for rubber goods and a committee of three, consisting of C. R. Boggs, C. E. Waters and G. H. Savage, was appointed to consider the question.

Great enthusiasm was shown throughout the meeting and there is every reason to hope that a strong and active Division of Rubber Chemistry may be formed. F. J. MAYWALD, *Secretary.*

All of the above minutes abstracted and edited from the originals which are held on file. CHARLES L. PARSONS,
Secretary Amer. Chem. Soc.

COUNCIL.

The requirement of the Post Office Department being that such portion of the payment made by members ascribed to membership dues should be entirely separated in our By-laws from the amount paid for subscriptions, the Council, after the required three weeks' notice, have unanimously voted to change By-laws 14:

> The annual dues of members shall be $2.50, the subscription charges for members subscribing to the publications of the Society shall be $7.50, both annual dues and subscription charges to be payable in advance on the first day of January of each year. Persons elected to membership after October of any year shall not be required to pay annual dues for that year.

to read:

> By-law 14.—The annual dues of members shall be $2.50, payable in advance on the first day of January of each year. Persons elected to membership after October of any year shall not be required to pay annual dues for that year. The payment of membership dues does not entitle the member to receive any of the publications of the Society entered by the Post Office Department as second-class matter.

and to have the subscription rates made and legalized by vote of the Directors instead of being a part of the By-laws.

The following changes in the By-laws have also been made by the Council to bring the By-laws into conformity with the requirements above mentioned:

> By-law 15.—Any newly elected member upon the payment of the subscription charges for the year in which he is elected shall be entitled to receive all the publications of the Society for that year.
>
> By-laws 16.—Any member in arrears for subscription charges for two months shall not thereafter receive the journals of the Society until all his arrears are paid.

Boston Meeting.

The Council met at the Hotel Lenox on Monday evening, December 27th, at 8.30 o'clock, with President Whitney in the chair and the following members present: W. R. Whitney, C. L. Parsons, H. P. Talbot, Edw. Bartow, S. W. Parr, Louis Kahlenberg, F. C. Phillips, Morris Loeb, L. P. Kinnicutt, W. D. Bancroft, Chas. Baskerville, C. H. Herty, Alfred

Springer, W. D. Richardson, A. Lowenstein (substitute for G. Thurnauer), M. T. Bogert, W. A. Noyes, G. C. Stone, G. P. Adamson, A. D. Little, A. A. Noyes, A. W. Browne (substitute for L. M. Dennis), Wm. Brady, R. S. Curtiss, L. H. Baekeland, W. R. Smith, Wm. McPherson, T. J. Parker, E. G. Love, W. F. Hillebrand, G. B. Frankforter, W. T. Taggart, Alex. Smith, J. H. Long, W. L. Miller, C. A. Catlin, L. A. Olney, A. M. Comey (substitute for G. E. Barton), A. P. Hallock, J. F. Norris and W. H. Walker.

It was voted that the President and the Secretary be empowered to arrange for the San Francisco Meeting and fix the date thereof.

It was voted that the report of the committee approving the By-laws of the Organic Division be accepted and the By-laws approved by the Council.

It was voted that a committee be appointed with power to pass upon the constitutionality of the By-laws submitted by the Division of Fertilizer Chemistry and to approve them for the Council. President Whitney has appointed H. W. Wiley, F. C Cameron, C. S. Hudson.

It was voted that the By-laws of the Division of Physical and Inorganic Chemistry be referred back to the Division to make two slight changes necessary to bring them into conformity with the Constitution and By-laws of the Society and that when these changes are made the By-laws be approved.

It was voted that a Directory of the Society be published during the summer months as a separate to be distributed to members and others under conditions laid down by the Directors of the Society which shall properly safeguard the use of the list from those who wish it for advertising purposes.

A motion having been made in regard to granting special privileges to undergraduate student members, it was voted to refer the matter to a committee to consider same and report back to the Council. President Whitney appointed A. A. Noyes, T. W. Richards and H. P. Talbot members of this committee.

It was voted that a paper be circulated by a committee appointed by the Chair to secure subscriptions to the fund for a monument to Marcelin Berthelot and that the amount of subscription received be sent as a contribution from the members of the Chemical Society and that if it does not reach one thousand francs, it be referred again to the Council The Chair appointed M. T. Bogert, Chas. Baskerville and W. Lash Miller

The following resolutions on the death of Charles Benjamin Dudley were presented by H. P. Talbot and unanimously adopted by the Council, all members rising.

Resolutions on the Death of Charles Benjamin Dudley.

In the death of Charles Benjamin Dudley, which occurred on December 21, 1909, the American Chemical Society has lost one of its most valued members, whether measured by the length of association with its affairs, by the wisdom and helpfulness of his counsel, or by his loyalty to its interests.

The Council of the Society desires to record its sense of deep appreciation of the services rendered to the Society by Dr. Dudley, both as a member from the time of its organization, as a long-time member of its Council and Board of Directors, and as its President.

By his professional accomplishments, especially in the field of applied chemistry, and in particular by his successful efforts to place the business relations between manufacturer and consumer upon an intelligent, accurate, and equitable basis, Dr. Dudley had won an enviable renown, fully recognized by the Council. This success was largely made possible by his high integrity, his quiet sense of equity, his courage in maintaining a carefully formed opinion and his uniformly lovable character—traits which also endeared him to all his associates, to whom his death brings a sense of personal loss.

The Council of the American Chemical Society votes, therefore, to spread this entry on its minutes and to extend its deep sympathy to the members of his family in their days of sadness.

It was voted that a committee be appointed by the President to consider the matter of the publication and distribution of papers read before the general meetings of the Society or its Local Sections when such papers are adjudged by the Editors for any reason unsuited for publication in the Journal, although of value and interest to members. The President appointed Francis C. Phillips, W. A. Noyes and H. P. Talbot.

The following committee report was then presented by A. D. Little, in the absence of Chairman Veitch and it was voted that the report be received, published in full in the Journal, and that the committee be retained and be thanked for its efficient work.

Report of the Paper Committee of the American Chemical Society.

December, 1909.

At the June meeting of the Society in 1908 at Mr. Veitch's request, Mr. Tolman laid before the Council some results which the former had obtained on the paper then used in the *Journal of the American Chemical Society* and *Chemical Abstracts*, which brought out the fact that this paper did not comply with the specifications, was of low quality and needlessly heavy and bulky. The Council, on motion of Mr. Tolman, appointed a committee consisting of Dr. W. A. Noyes, Dr. McMurtrie, Mr. A. D. Little, Mr. M. L. Griffin and Mr. Veitch to "consider the quality of the paper used in the Journals" and to secure, if practicable, more suitable papers. The committee worked under difficulties. The funds of the Society were limited and therefore the total cost of printing and mailing the journals could not be increased, and, furthermore, as the members of the committee live in different parts of the country most of its work has been done through correspondence with its attendant delays.

In the execution of its duties it has been the purpose of the committee to secure the most durable, strongest, lightest, thinnest, most opaque and cleanest paper, having a surface not injurious to the eyesight, that it was possible to procure for the money available.

The problem is complicated by the fact that certain characteristics which a paper should have are diametrically opposed to other equally, or more, important qualities. Thus lightness and thinness are secured at the expense of opacity, while opacity means greater thickness and weight, or less strength and durability. In a paper of a given weight and thickness opacity is secured at the sacrifice of strength and durability; lightness and thinness are secured at the sacrifice of strength, durability and opacity. It is evident, therefore, that any paper must be a compromise among opposing characteristics and the nature of this compromise is determined by the purpose for which the paper is to be employed In effecting this compromise the committee steadily endeavored to maintain essentials and to accentuate utility. The committee recognizes that there are members of the Society who would much prefer what they would declare is a better-appearing paper, one that is thicker, stiffer and less transparent. This view has not been ignored by the committee. It is believed, however, that the briefest consideration of the subject and the most cursory comparison of the current issues, particularly the bound volumes, with those of last year will furnish convincing evidence in support of the action of the committee.

The advantages of the paper used this year are at once apparent. The current volume of *Chemical Abstracts* will be bound in two, while the 1908 issues were bound in three volumes, a saving of one-third on the cost of binding. The shelf space and weight per volume of the same number of pages is also reduced approximately one-third. The publications are much more convenient to handle, and are more safely and economically stored, both important considerations to the reader and to the librarian.

It was difficult to secure an acceptable paper at a price which the Society could pay. The specifications are more stringent than it is customary to draw for paper of this class. Paper-makers prefer to make heavier and thicker paper, as more can be produced for the same operating expenses, and further, the printer feared the new paper would not work satisfactorily on the presses, and urged that no change be made. All of these difficulties and objections were finally overcome and a paper made to comply with the following specifications was secured:

Stock.

Rag	75 per cent.
Bleached chemical wood or equivalent thereto	25 "
Ash—China clay	5 "
Weight (26 × 38, 500)	42 pounds.
Strength (Mullen)	15 "
Folding number (Schopper) if practicable	10 "

Sizing $^3/_4$ rosin—no starch.
Finish—uniform machine, same on both sides.
Color—uniform, natural.
Paper must be well washed to remove soluble salts and bleaching materials.

The comparative value of the old and new papers is shown except so far as opacity is concerned, by the following statement of the composition, strength, and folding qualities of the papers:

Stock.	Old.	New.
Rag	20 per cent.	77–81
Bleached chemical wood	80 "	23–19
Ash	12–20 "	6.4–8.7
Weight—ream 26 × 38, 500 lbs	60 "	40–42
Thickness, thousandths inch	3.8 "	3.0
Double folds (weak direction)	2 "	3–4
Strength, Mullen	5–10 pounds.	12–14.5

From these specifications it is clear that the paper now used is much superior in durability and strength to that formerly used and it was estimated would cost no more for a year's supply. In confirmation of the opinion of the committee on the question of cost it may be interesting to know that in a letter to Dr. Noyes, dated February 4, 1909, the printer states that the postage on the foreign-going February issue of the Journal was $10.50 less than it would have been if printed on the old paper and the domestic postage was $10.00 less, a total saving in postage of $20.50 on the February issue. The paper for this issue, however, cost $13.20 more than the old paper would, reducing the net saving on the new paper to $7.30. If this rate extends throughout the year on the three monthly issues of the Journal and Abstracts, the new paper, in addition to the other advantages, will have saved the Society approximately $200 per year. Doubtless the editors can give definite information on this point.

The committee has endeavored to improve this paper for 1910. It is fully realized that it will not withstand indefinitely the severe usage of library reference, such as the publications of the Society are subjected to. So far, however, improvement has not been feasible, except that the opacity has been increased by increasing the ash from 5–8 per cent. The cost of the paper has been reduced from 6.84 cents to 6.55 cents per pound.

It has not been the object of the committee to have the publications cost less, however, and though the same paper at a materially lower cost has been selected for next year's issues, the committee hopes ultimately to secure a much better paper which which may cost more.

During this year the committee has, after consultation with and the approval of Mr. Richardson, the editor, drawn the following specifications for the paper for the "Engineering and Industrial Journal":

Stock.	
Rag	60 per cent.
Bleached chemical wood or equivalent thereto	40 "
Ash	15 "
Weight, ream	100 pounds.
Thickness thousandths inch, maximum	0.0032
Strength, Mullen	15 pounds.

Sizing, rosin, no starch.
Finish, uniform, supercalendered, same on both sides.
Color, uniform, natural.
Paper must be well washed to remove soluble salts and bleaching materials.

The comparative value of the paper in the current volume and the proposed paper is indicated in the following table:

Stock.	Present paper.	New paper.
Rag	38–60 per cent.	60 per cent.
Bleached chemical wood	62–40 "	40 "
Ash	16–26.7 "	15 "

	Present paper.	New paper.
Weight ream 35 × 48, 500	120 pounds.	100 pounds.
Thickness, inch	0.0035–0.0040	0.0032
Strength, Mullen	9–14 pounds	15 pounds.
Double folds	1–2 "	not det'n.
Sizing	rosin.	rosin.

In other words, the new paper will be of better stock, will be stronger, thinner, lighter, contain less loading and will as a consequence prove more durable in service. The improvements are along the lines followed in the Journal paper, but the changes will not be so marked. The committee estimates that the saving in printing and mailing the "Industrial Journal" will approximate $200 per annum.

Consideration has been given the cover paper used on the Society's publications. It is reasonably certain that better and at the same time less expensive covers can be had. A suggestion that more distinctive colors be given the covers of the several publications has been made and the committee has the whole question of covers under consideration, upon which a decision may be reached in time for the 1910 issues.

It may not be out of place to call attention to the fact that owing to the continued deficit in the Post Office Department, serious consideration may be given by this Congress to the proposal to increase the postage on second-class matter. Should this be done the effect on the finances of the Society will be less serious than if a heavier paper were employed in its publication.

In closing this report of progress your committee would emphasize again the fact that its efforts have been against the modern print paper making practice, which emphasizes quantity rather than quality. Final results are not therefore obtained at once.

Better and more suitable paper than that so far secured for the publications of the Society can undoubtedly be obtained at once at considerably increased cost. It is believed that in time better paper may be had, at but small increase in cost. When paper makers in general are more familiar with the manufacture of this class of paper, when they become better acquainted with modern methods of paper testing and know more definitely what tests their products will comply with, there will doubtless be more competition and higher grade paper can be secured. It would seem advisable, therefore, if it meets with the wishes of the Council, to continue the committee to this end.

In conclusion it may be said that from the utilitarian viewpoint, and probably from the artistic as well, the publications of the Society have been improved and the expense of printing them materially reduced.

It was voted that W. D. Richardson and A. M. Patterson be added to the committee on paper.

The Treasurer's report was read and adopted.

It was voted that the Budget for 1910 be taken up and considered by sections.

It was voted that the question of policy in conducting the *Journal of Industrial and Engineering Chemistry* be referred to the Executive Committee of the Division of Industrial Chemists and Chemical Engineers for an expression of opinion with the request that they consider the matter and send their opinion to the Council on Wednesday evening.

It was voted that when the meeting adjourned it adjourn to reconvene immediately following the President's address on Wednesday evening.

It was voted that the question of expenses of officers and editors attending the meetings of the Society hereafter be referred to a committee to report on Wednesday evening.

Several items of the Budget were then passed and others discussed and the whole was left over for final approval as a whole for the next meeting of the Council.

The President appointed as a committee to consider the matter of expenses of officers attending meetings of the Society, Morris Loeb, W. D. Bancroft and Wm. McPherson.

A second Council meeting was held Wednesday evening, December 29th, following the President's address. The meeting was called to order with the following members present: W. R. Whitney, F. B. Carpenter, A. P. Hallock, G. P. Adamson, H. W. Wiley, A. D. Little, L. P. Kinnicutt, C. A. Catlin, G. B. Frankforter, R. E. Stallings, A. W. Browne (substitute for L. M. Dennis), A. B. Stevens, F. C. Phillips, C. L. Parsons, J. E. Mills, W. A. Noyes, J. H. Long, H. P. Talbot, Alex. Smith, W. D. Bancroft, W. D. Richardson, M. T. Bogert, Morris Loeb, E. G. Love, T. J. Parker, W. F. Hillebrand, L. A. Olney, W. R. Smith, G. C. Stone, Edw. Bartow, L. H. Baekeland, C. H. Herty, Wm. Brady, Chas. Baskerville, Alfred Springer, W. T. Taggart, S. W. Parr, A. Lowenstein (substitute for G. Thurnauer).

It was voted that the present committee in charge of the Section of Chemical Education be continued.

It was voted that the Program Committee be instructed by the Council to comply if possible with the recommendations of the committee having in charge the Section of Chemical Education to the effect that when the Section of Chemical Education arranged a program bearing especially upon the work of one of the Divisions a free half-day for the program the Section of Chemical Education be found upon which the Division concerned shall hold no program of its own, leaving it in the jurisdiction of the Program Committee, however, to arrange the matter as may be most satisfactory.

The Executive Committee of the Division of Industrial Chemists and Chemical Engineers presented their opinion in regard to the policy to be followed in conducting the *Journal of Industrial and Engineering Chemistry* as requested at the previous Council meeting. As a result of their recommendations the following motions based thereon were passed:

Voted, That all papers giving the results of good research work that are offered or can be obtained be published within the limits of the appropriated Budget.

Voted, That in addition to papers on original work others dealing with progress in any given line or with improvements or processes should be published and that three hundred dollars or as much thereof as may be necessary be appropriated for the period of six months to be used in the discretion of the editor in procuring articles coming under this recommendation.

Voted, That the question of printing the Journal throughout in 9-point type be referred to the directors with power.

Voted, That the editor of the *Journal of Industrial and Engineering Chemistry* be paid a salary of one thousand dollars per year and 5 per cent. on the advertisements secured by him up to the time an advertising agent is appointed.

Voted, That a committee of five be appointed by the chair to recommend to the directors a suitable advertising agent for employment and that W. D. Richardson and Wm. McMurtrie be members of the committee. President Whitney appointed A. D. Little, W. D. Richardson, Wm. McMurtrie, W. H. Walker and Geo. P. Adamson.

Voted, That the Board of Directors upon such recommendation from the committee be authorized to employ an advertising agent on a commission basis, such commission not to exceed 25 per cent.

It was voted that the question of publishing a separate *Journal of Agricultural and Food Chemistry* be referred to a committee to be selected by the President of the Society in conjunction with the Executive Committee of the Division of Agricultural and Food Chemistry and that copies of the report of this committee be sent to all members of the Council by mail not later than June 1, 1910.

Dr. Loeb reported for the committee appointed at the previous meeting to make recommendations in regard to the expenses of officers at General Meetings and the following recommendations of the committee were unanimously adopted.

1. That the railroad and hotel expenses of the President and the Secretary be paid at both the annual and the summer meeting.
2. That the traveling expenses be paid for the Treasurer and Editors in attendance at the annual meeting.
3. That if the Board of Directors desire to present a special recommendation to the Council at a summer meeting which affects the work of one of the officers, such officer shall be previously notified and if he desires to be heard in opposition shall be paid his traveling expenses.

It was voted that the item of clerical expense for the Editor of the *Journal of Industrial and Engineering Chemistry* be referred to the Directors with power to arrange as necessary after consultation with the Editor.

It was voted that the item for printing pages of advertisements in the *Journal of Industrial and Engineering Chemistry* be struck out of the Budget as a contingent item and be referred to the Board of Directors with power.

It was voted that the Board of Directors be requested if possible to submit the Budget each year to the Council by mail in advance of the meeting.

It was voted that the Treasurer be paid a salary of two hundred dollars a year and that this item be added to the Budget.

It was voted that the following Budget as a whole be referred to the

Board of Directors with the recommendation that it be passed by them in conformity with the acts of this meeting.

Budget for 1910.

RECEIPTS.

Dues	$42,000.00
Advertisements	6,500.00
Subscriptions	2,500.00
Postage	500.00
Back numbers	1,000.00
Interest	500.00
	$53,000.00

EXPENDITURES.

Journal American Chemical Society:		
Editor's salary	$ 1,000.00	
Expenses	200.00	
Reviews	100.00	
Printing	7,070.00	
Reprints (net)	350.00	
Total		8,720.00
Chemical Abstracts:		
Editor's salary	$ 1,000.00	
Associate editor, salary	867.00	
Assistance, including indexer	1,583.00	
Expenses	450.00	
Abstractors	4,700.00	
Printing, including index	14,650.00	
Total		23,250.00
Journal of Industrial and Engineering Chemistry:		
Editor salary	$ 1,000.00	
Printing 850 pages at $6.20 per page	5,270.00	
Printing advertisements[1]		
Authors' reprints, $50 per month	600.00	
Index	100.00	
Postage, $20.00 per month	240.00	
Expense	600.00	
Clerical[2]		
Special expense[3]	300.00	
Total		7,810.00
Commission: advertising, at 20 per cent.		1,300.00
collections, at 4 per cent		1,840.00
Secretary's office:		
Clerical		1,200.00
Expense		1,250.00

[1] Referred to directors.

[2] Appropriation covering first six months.

[3] The item of clerical expense has been left to the directors with power. The editor estimates that $60 per month will be required until such time as he is relieved of the advertising and $30 per month thereafter.

Treasurer's office:	
Salary	200.00
Expense	400.00
President's office	50.00
Librarian's office	500.00
General meetings	1,500.00
Local sections	2,500.00
Incidentals	800.00
Back numbers	500.00
Directory	350.00
Total	$52,170.00
Contingent items (noted in foot-notes) estimated 120 pages advertisement Jour. I. & E. C.	744.00
Clerical, Editor of Jour. I. & E. C.	420.00
Grand total	$53,334.00

It was voted that the title of the general Committee on Uniformity of Technical Analysis be changed to the Committee on Standard Methods of Analysis.

It was voted that the Committee on Standard Methods of Technical Analysis of the Division of Industrial Chemists and Chemical Engineers be constituted a subcommittee of the Committee on Standard Methods of Analysis, and that the Chairman of the said Committee of the Division of Industrial Chemists and Chemical Engineers be a member of the general committee with right to vote limited to matters relating to the work of his own committee.

It was voted that all committees similarly constituted to standardize methods of analysis be likewise made subcommittees of the Committee on Standard Methods of Analysis.

The following officers were then elected: *Directors for two years*, A. D. Little, E. G. Love. *Finance Committee*, E. G. Love, P. C. McIlhiney, G. C. Stone. *Membership Committee*, Wm. McMurtrie, E. G. Love, B. E. Curry. *Secretary*, Charles L. Parsons. *Treasurer*, Albert P. Hallock. *Librarian*, Daniel D. Berolzheimer. *Editors*: *Journal of the American Chemical Society*—W. A. Noyes, *Editor-in-Chief*; M. T. Bogert, Edward Hart, W. F. Hillebrand, J. H. Long, Arthur A. Noyes, Charles L. Parsons, H. P. Talbot, H. W. Wiley. *Chemical Abstracts*—A. M. Patterson, *Editor-in-Chief*; J. J. Miller, *Associate Editor*. *Journal of Industrial and Engineering Chemistry*—W. D. Richardson, *Editor-in-Chief*; Geo. P. Adamson, E. G. Bailey, G. E. Barton, Wm. Brady, Wm. Campbell, F. B. Carpenter, Virgil Coblentz, Francis I. Dupont, W. C. Ebaugh, Wm. C. Geer, W. F. Hillebrand, W. D. Horne, L. P. Kinnicutt, A. E. Leach, Karl Langenbeck, A. D. Little, P. C. McIlhiney, E. B. McCready, Wm. McMurtrie, J. Merritt Matthews, T. J. Parker, J. D. Pennock, G. C. Stone, F. W. Traphagen, Ernst Twitchell, Robert Wahl, Wm. H. Walker, M. C. Whitaker, W. R. Whitney.

W. D. Bancroft having been elected President and also Councilor-at-Large, it devolved upon the Council to elect a Councilor in his place and W. L. Dudley, of Nashville, Tenn., was elected Councilor-at-Large for three years from January 10, 1910.

It was voted that the vacancies on the Board of Editors of the *Journal of Industrial and Engineering Chemistry* be referred to the Executive Committee of the Division of Industrial Chemists and Chemical Engineers with power to fill same and that any other vacancies occurring between meetings be likewise treated.

The committee appointed at the previous meeting to consider the publication of papers other than those printed in the Society's Journals reported but after considerable discussion the report, mainly for financial reasons, was tabled.

It was voted unanimously that the Council express its appreciation to Dr. E. G. Love for his long and faithful services as Librarian of the Society.

It was voted the Council express to Dr. Wm. McMurtrie their sincere congratulation on the recovery of his health and the hope that he may soon be able to meet with them again.

It was voted that the Council express their sincere thanks and appreciation to the authorities of the Ohio State University, the University of Illinois and the New Hampshire College for the courtesies which those institutions are extending to the Editor of *Chemical Abstracts*, to the Editor of the *Journal of the American Chemical Society* and to the Secretary.

It was voted that the thanks of the Council be extended to all the officers of the Society who have served them so faithfully during the past year.

It was voted that the Editor of *Chemical Abstracts* be made Chairman of the Committee on Exchanges and that the committee consist of the Editors of the Society's Journals and the Librarian.

It was voted that the Council meetings called at the time of the Annual Meeting of the Society shall begin at 2.30 o'clock on the afternoon preceding the opening session.

Adjourned.

CHARLES L. PARSONS,
Secretary.

MEMBERS ELECTED BETWEEN DEC. 15, 1909, AND JAN. 15, 1910.

Alkier, S. J., 6 Sumner Ave., Brooklyn, N. Y.
Allard, M. L., c/o Gutta Percha & Rubber Mfg. Co. of Toronto, Toronto, Can.
Allwood, Wm. H., 484 Broadway, Everett, Mass.
Babington, Fred W., Customs Lab'y, Ottawa, Canada.
Bahe, William, 426 McKean St., Philadelphia, Pa.
Bainbridge, Edmund F., 283 Congress St., Bradford, Pa.

Barrett, Edward P., Rolla, Mo.
Bausch & Lomb Optical Co., Rochester, N. Y.
Beard, Stanley D., 449 East 57th St., New York City.
Biach, Ludwig K., Norwich, Conn.
Bird, Roy J., Orono, Maine.
Blake, Alfred E., Durham, N. H.
Boogs, Charles R., Simplex Electric Co., Cambridge, Mass.
Boren, Earl E., 402 Larimer Ave., Pittsburg, Pa.
Bower, John H., 2–6th St., N. E., Washington, D. C.
Bradley, Linn, 2104 Vermont Ave., So. Los Angeles, Calif.
Bradley, Walter M., 520 Whitney Ave., New Haven, Conn.
Brann, Bertrand F., 227 Essex St., Bangor, Maine.
Brautlecht, Charles A., 38 Clark St., New Haven, Conn.
Breckenridge, James M., 325 W. Dayton St., Madison, Wis.
Breuning, Wm. H., 1401 East 55th St., Chicago, Ill.
Brewer, Howard D., 4 Congress St., Worcester, Mass.
Burwell, Albert L., Winsted, Conn.
Chase, Edward S., 208 N. 4th St., Reading, Pa.
Childress, Geo. C., Knoxville, Tenn.
Clapp, Dudley, 52 Hartford St., Dorchester, Mass.
Clark, Robert H., Clark University, Worcester, Mass.
Cleveland, D. B., 1856 East 63rd St., Cleveland, Ohio.
Coleman, Wm. B., 113 South 37th St., Philadelphia, Pa.
Collins, Lawrence M., Washington and Lee Univ., Lexington, Va.
Comstock, Laura (Miss), Orono, Maine.
Conarroe, Alvin N., 1603 St. Charles Road, Maywood, Ill.
Cone, Lee H., 1216 Prospect St., Ann Arbor, Mich.
Cook, Edwin F., 743 N. New Jersey St., Indianapolis, Ind.
Cornell, Sidney, 134 North Second St., Duquesne, Pa.
Cummins, Earl H., 1332 6th Ave., Des Moines, Ia.
Curme, George O., Jr., 45 Conant Hall, Cambridge, Mass.
Cutler, D. A., c/o Revere Rubber Co., Chelsea, Mass.
Davidson, D. McL., 804 Nichols St., Fulton, Mo.
Davis, John R., Box 102, Bridgeville, Pa.
Davis, Myron P., 2nd, 1112 13th Ave., Altoona, Pa.
Dedrick, Charles H., Williamsburg, Pa.
Denny, Henry W., State Lab'y of Hygiene, Trenton, N. J.
Doggett, Lucy F. (Miss), Ill. Food Lab'y, 1623 Manhattan Bldg., Chicago.
Durgin, Cora A. (Miss), 38 Clifton St., Worcester, Mass.
Eby, John G., 1711 W. Susquehanna Ave., Philadelphia, Pa.
Edwards, J. D., 2244 Nicollet Ave., Minneapolis, Minn.
Emery, Sidney S., Louviers, Douglas Co., Colorado.
Engle, S. G., 704 Conn. St., Gary, Ind.
Eve, J. Hammond, c/o Southern Cotton Oil Co., Savannah, Ga.
Fagan, James P., Berlin, N. H.
Fairbank, The N. K. Co., 143 Dearborn St., Chicago, Ill.
Fales, Almon L., 13 Jaques Ave., Worcester, Mass.
Fels & Co., Philadelphia, Pa.
Fisher, Henry D., c/o Factory K. U. S. Glass Co., Pittsburg, Pa.
Fulweiler, W. Herbert, Moylan, Delaware Co., Pa.
Glass, John W., 1515 So. 8th St., Terre Haute, Ind.

Glaze, John B., 530 Massachusetts Ave., Boston, Mass.
Goodrich, Charles C., 2 Rector St., New York City.
Hall, Clarr H., 177 14th St., Milwaukee, Wis.
Hamilton, Paul B., c/o The Oakes, Windsor Park, Chicago, Ill.
Harney, John M., 24 East Hill St., Wabash, Ind.
Hayward, J. C., 603 East Seneca St., Ithaca, N. Y.
Heim, Wm. L., 115 Biddle St., Kane, Pa.
Heise, George W., 1022 Park St., Grinnell, Ia.
Heller, Harry, c/o Great Western Sugar Co., Loveland, Colo.
Henderson, V. E., University of Toronto, Toronto, Canada.
Henry, David H., Clemson College, So. Car.
Hirsch, Alcan, 142 Beacon St., Boston, Mass.
Hoffmann, George L., 359 Vine St., W. Lafayette, Ind.
Holladay, J. Albert, 442 Seneca St., So. Bethlehem, Pa.
Holliday, Karl J., Akron Apartments, Pittsburg, Pa.
Hopp, G., 122 Catharine St., Ithaca, N. Y.
Houston, Dwight, M., 921 Winchester St., Milwaukee, Wis.
Houston, John R., c/o Filer & Stowell Co., Milwaukee, Wis.
Hutchison, Charles F., c/o Eastman Kodak Co., Kodak Park, Rochester, N. Y.
Hyde, Austin T., Rumford, Maine.
Jacob, J. E., Ancon Hospital, Canal Zone.
Janitzky, Emanuel J., Box 135, Duquesne, Pa.
Jenne, Lyle L., 120 E. Washington Lane, Philadelphia, Pa.
Johnson, L. D., 202 Williams St., Ithaca, N. Y.
Jonas, Horace, N., Michigan St., Racine, Wis.
Jones, Howard M., 504 City and County Bldg., Salt Lake City, Utah.
Jungersen, Ole H., 2853 91st St., Chicago, Ill.
Kent, Arthur G., c/o Nat'l Calfskin Co., Peabody, Mass.
Kipp, Orrin L. G., Ames, Iowa.
Klar, Max, 5 Kantstrasse, Hannover, Kleefeld, Germany.
Kline, C. Erle, Melrose Park, Montgomery Co., Pa.
Kostalek, John A., 1001 So. 5th St., Champaign, Ill.
Kratz, G. D., 526 Stewart Ave., Ithaca, N. Y.
Kraybill, B. E., Orono, Maine.
Lafferrander, Robert L., 129 York St., Brooklyn, N. Y.
Laftman, Axel B., c/o Grasselli Chem. Co., Grasselli, N. J.
Lascoft, J. Leon, 1223 Lexington Ave., New York City.
LaShell, Lewis L., 210 Waverly St., Warren, Ohio.
Lehmann, Adolf L. J., Strathcona, Alberta, Canada.
Lewis, George C., New Dorp, Staten Island, N. Y.
Libby, S. W., 6 Olive St., Watertown, Mass.
Lilly, The Eli & Co., Indianapolis, Ind.
Lloyd, Hoyes, 396 Brunswick Ave., Toronto, Canada.
Lyon, Clarence H., 1047 Waverly Ave., Kansas City, Kans.
Mann, Charles A., 924 Clymer Place, Madison, Wis.
Marshall, Charles E., East Lansing, Mich.
Martin, James H., 244 E. Broadway, Winchester, Ky.
Mason, Thos. W., 304 W. Spring St., Northfield, Minn.
McAbee, W. D., 5 The Griffith, Indianapolis, Ind.
McKenney, R. E. B., Cosmos Club, Washington, D. C.
Meader, John W., 705 Greer St., Indianapolis, Ind.

Mighill, Thomas A., 15 Exchange St., Boston, Mass.
Moat, Charles P., 184 Church St., Burlington, Vt.
Moore, C. J., 522 26th Ave., S., Seattle, Wash.
Moore, H. C., 53 W. Baker St., Atlanta, Ga.
Moore, Philip A., 630 So. Randolph St., Champaign, Ill.
Mowry, Leland B., Nayata Lodge, Cayuga Heights, Ithaca, N. Y.
Nicholson, A. R., Wyncote, Pa.
Nuckolls, A. H., 6325 Monroe Ave., Chicago, Ill.
Oberfell, Charles R., Harrisonburg, Va.
Patterson, Romney C., 201 Oak Ave., Ithaca, N. Y.
Peel, Charles E., Durham, N. H.
Pennsylvania Rubber Co., Jeannette, Pa.
Pettijohn, Earl, 2314 Langford Ave., Minneapolis, Minn.
Pickel, George J., St. Ignatius College, Cleveland, Ohio.
Pierce, E. G., 60 College House, Cambridge, Mass.
Plummer, Fred B., University of Chicago, Chicago, Ill.
Porter, A. H., New Prague, Minn.
Rassow, B., Stephanstr. 18, Leipzig, Germany.
Rathjen, Edwin F., 121 Maple Ave., Ithaca, N. Y.
Richards, W. A., University High School, Univ. of Chicago, Chicago, Ill.
Roebling, Herman, 630 Lake St., Madison, Wis.
Rollin, Charles, 1 St. Nicholas Buildings, Newcastle-on-Tyne, Eng.
Rosino, Gilbert G., 169 West 11th Ave., Columbus, Ohio.
Ruskowsky, Fred A., 8923 Houston Ave., Chicago, Ill.
Schneeberg, Bertrand, 1026 Broadway, Camden, N. J.
Scott, E. H., Milledgeville, Ga.
Scott, Grant E., 439 College St., Burlington, Vt.
Shaw, L. I., 271 Langdon St., Madison, Wis.
Shengle, John C., c/o Kiangsu Chem. Wks., Shanghai, China.
Showalter, Ralph W., 3338 N. Illinois St., Indianapolis, Ind.
Silverthorn, James C., 1131 Broadway, Albany, N. Y.
Sims, James M., 7423 Railroad Ave., Chicago, Ill.
Slocum, Harry E., 118 Craft Ave., Pittsburg, Pa.
Smith, George A., 1069 Prospect Place, Brooklyn, N. Y.
Snell, Walter R., Dubois, Pa.
Spears, Howell D., Ky. Exper. Station, Lexington, Ky.
Sprague, Forest O., Rear 208 Summer St., Boston, Mass.
Stack, E. B., Monroe, No. Car.
Steward, R. F., 1768 Columbia Road, Washington, D. C.
Strachan, E. K., 410 E. Chalmers St., Champaign, Ill.
Strickland, F. P., Jr., 2101 N. 5th St., Kansas City, Kans.
Swan, Harry B., 1155 Sycamore St., Buffalo, N. Y.
Taylor, John, Liggett Bldg., St. Louis, Mo.
Taylor, Richard R., 474 Mass. Ave., Boston, Mass.
Thayer, Harry M., c/o The Proctor & Gamble Co., Kansas City, Kans.
Titus, Martin E., 733 3rd St., Milwaukee, Wis.
Tuttle, Herbert C., 17 Gramercy Park, New York City.
Van Haagen, Walter K., Ga. School of Technology, Atlanta, Ga.
Welles, Arthur T., 2 Magee Ave., Rochester, N. Y.
Whealdon, Albert D., Superior, Wis.
Whitcomb, J. A., 121 Paulison Ave., Passaic, N. J.
Wilber, David T., 321 Dryden Road, Ithaca, N. Y.

Will & Baumer Co., Syracuse, N. Y.
Wills, Frank, 505 E. Green St., Champaign, Ill.
Wilson, Edgar P., 123 Woodland Ave., New Rochelle, N. Y.
Woods, Charles S., 327 Newton Claypool Bldg., Indianapolis, Ind.
Woodyatt, Rollin T., Rush Medical College, Chicago, Ill.

BOARD OF DIRECTORS.

A meeting of the Board of Directors was held at the Hotel Lenox at 1.30 A.M., Thursday, December 30th, with Messrs. Whitney, Bogert, Parker, Hallock and Parsons present.

A quorum being announced, it was voted that all the recommendations of the Council with regard to financial matters as recorded in the minutes of the Council for December 27, 1909, and December 29, 1909, are hereby approved and adopted as the action of the Board of Directors.

Adjourned. CHARLES L. PARSONS,
Secretary.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

PITTSBURG SECTION.

The regular meeting of the Section was held at the Carnegie Technical Schools, Applied Science Building, on Thursday evening, December 16th, at 8 o'clock.

The program included the following papers: "Some Improved Gas Analysis Apparatus," by Dr. E. J. Hoffman, U. S. Geol. Survey. "The Determination of the Percentage of Phosphorus Retained with the Ferric Chloride in the Ether Separation," by R. J. Wysor, Chemist, Carnegie Steel Co. "The Analysis of Explosives," by Dr. Walter O. Snelling, U. S. Geol. Survey. JOHN A. SCHAEFFER, *Secretary.*

SECTION OF EASTERN NEW YORK.

The October meeting was held at Schenectady on Friday, October 15, 1909, at 8 P.M., in the parlors of the New Vendome Hotel. Dr. M. A. Hunter spoke on the subject "The Natural Resources of New Zealand," relating some observations of his recent trip to the Southern Pacific.

The December meeting was held at the Rensselaer Polytechnic Institute, Troy, on Friday evening, December 17, 1909, at 8 o'clock. Dr. A. T. Lincoln gave a paper on "The Hydrate Theory of Solutions."

The Troy ladies served refreshments at the close of the program.

The following officers were elected for 1910: *President*, Edward Ellery, Union Univ., Schenectady; *Vice-President*, John Hurley, Little Falls, N. Y.; *Secretary-Treasurer*, R. C. Robinson, Res. Lab., G. E. Co.; *Councilor*, M. A. Hunter, R. P. I., Troy *Advisory Committee*, A. T. Lincoln, R. P. I., Troy; W. R. Whitney, Schenectady; F. C. Zapf, 335 McClellan St., Schenectady.

F. C. ZAPF, *Retiring Secretary.*

The January meeting was held in the Chemical Lecture Room of Union College, on Friday evening, January 7th, at 8 o'clock.

Dr. C. F. Hale, of the Research Laboratory of the General Electric Co., gave a paper on "Recent Advances in the Liquefaction of Gases," illustrated with lantern slides and experiments.

Business meeting and refreshments followed.

R. C. ROBINSON, *Secretary.*

WISCONSIN SECTION.

At the annual meeting of the Section held December 8, 1909, the following officers were elected for the year 1910: *Chairman,* E. B. Hart; *Vice-Chairman,* Richard Fischer; *Councilor,* H. C. Bradley; *Secretary,* E. V. McCollum; *Treasurer,* W. F. Koelker.

FRANCIS C. KRAUSKOPF, *Retiring Secretary.*

The January meeting was held at Madison on Wednesday, January 12th, at 8 P.M. in the Chemistry Building Professor W. F. Koelker presented a paper on "The Utilization of the Amino Acids and Polypeptids by the Tubercle Bacillus."

Following the paper there was an informal discussion of the Boston Meeting of the Chemical Society by Professors Kahlenberg, Bradley and Loevenhart.

E. V. MCCOLLUM. *Secretary.*

INDIANA SECTION.

The Section met Friday evening, December 10, 1909, at 7.15 o'clock, at the office of the State Food and Drug Laboratory. The following papers were read: "Concerning the Decomposition of Uric Acid by Enzymes," Clarence E. May; "Boiler Water in Railway Service," J. R. Francis; "Scientific Treatment of the Problem of Cutting a Brilliant of Any Transparent Material," F. B. Wade; "Morphine Determinations," A. D. Thorburn.

A. D. THORBURN, *Secretary.*

IOWA SECTION.

The December meeting was held in Iowa City on December 11, 1909. The forenoon was given over to the reading of papers and discussions. After a dinner at the Burkeley Imperial, the meeting adjourned to inspect the plant for the electrolytic bleaching of flour recently installed in a local flour mill. The following papers were presented: "The Estimation of Cobalt and Arsenic in Smaltite," Nicholas Knight. "Nitrogenous Excretion," Miss Stella Hartzell. "Metallic Tellurites," Edward Wolesensky. "Delicate Tests for Cobalt in the Presence of Nickel and Iron," W. J. Karslake. "Colloidal Solutions," J. N. Pearce. "Bleaching of Flour," E. W. Rockwood.

J. NEWTON PEARCE, *Secretary.*

ST. LOUIS SECTION.

The regular monthly meeting was held on Monday evening, December 13th, at the Academy of Science Building. The following were elected officers for the year 1910: *President*, Prof. Edward H. Keiser; *Vice-President*, Dr. Charles E. Caspari; *Secretary*, Mr. R. Norris Shreve; *Treasurer*, Dr. Samuel H. Baer; *Councilor*, Mr. H. E. Wiedemann.

Mr. H. E. Wiedemann read a paper on "The Relation of Chemistry and Chemical Engineering to the Conservation of Our Natural Resources."

LEROY MCMASTER, *Retiring Secretary.*

The St. Louis Section met in conjunction with the St. Louis Chemical Society on January 10th. Messrs Alfred L. Kammerer and E. B. Fulks read a paper on "Timber Preservation." This paper, in the nature of a review of the work done by the railroads on this subject, was well illustrated by lantern slides. Mr. H. E. Wiedemann gave a résumé of the Boston meeting of the general society.

R. NORRIS SHREVE, *Secretary.*

LOUISIANA SECTION.

The thirty-sixth regular meeting was held on Friday evening, December 17th, in the Director's Room of the New Orleans Board of Trade. President F. C. Johnson presided. Dr. J. C. Mims presented a paper on "Waste Products." The usual discussion followed the reading of the paper and brought out some very interesting facts in regard to local trade problems.

W. L. HOWELL, *Secretary.*

NEW YORK SECTION.

The third regular meeting of the Session of 1909-'10 was held at the Chemists' Club, on Friday evening, December 17th. The following members were elected Councilors for the ensuing year: Morris Loeb, E. G. Love, Geo. C. Stone, L. H. Baekeland, T. J. Parker, W. D. Horne, Chas. Baskerville. The papers read were as follows: "Analyses of Some Antique Bronzes," Morris Loeb and L. R. Morey. "The Action of Radium Salts upon Ruby," Chas. Baskerville. "Apparatus for Drying Flasks," Chas. Baskerville and Reston Stevenson.

The fourth regular meeting of the Session of 1909-'10 was held at the Chemists' Club on January 7th. The program was as follows: "The Origin of the Chemical Elements," Henry B. Russell. "Chemical Examination of Watermelon Seed," and "Chemical Examination of Pumpkin Seed," F. B. Power and A. H. Salway. "Further Researches in the Quinazoline Field," C. G. Amend and M. T. Bogert.

C. M. JOYCE, *Secretary.*

UNIVERSITY OF ILLINOIS SECTION.

The regular December meeting was held at the Chemistry Building, December 21, 1909. The following papers were presented: "The Heat of Solutions of Metals in Acids," Dr. L. L. Burgess. "The Effect of

External Conditions upon the Physiological Activities of Some De-nitrifying Organisms." Dr. J. H. Petit.

L. H. SMITH, *Secretary.*

SYRACUSE SECTION.

The 54th regular meeting was held Friday evening, December 17th, at 8 P.M., in the Lecture Room of the Y. M. C. A.

The papers presented were as follows: "Invertase," by C. S. Hudson, Washington, D. C. "Some New Electrochemical Processes," by E. H. Archibald. "An Electric Gas Meter," by E. C. Scott. "Report of the Recent Convention of Chemical Engineers," by W. M. Booth.

The fifty-fifth regular meeting was held Friday evening, January 7, 1910, at 8 P.M. in Bowne Hall, Syracuse University. Professor Julius Stieglitz, from the University of Chicago, delivered an experimental lecture on "The Electrical Theory of Oxidation and Reduction."

An informal dinner was served at Sims Hall, Friday at 6.30 P.M., just preceding the lecture.

WM. H. MCLAUCHLAN, *Secretary.*

CINCINNATI SECTION.

At the December meeting of our Section Mr. Jerome K. Alexander, of New York City, addressed the members on the Ultra-microscope and demonstrated its use.

The 156th meeting of the Section was held on Wednesday evening, January 12th, at 8 o'clock, in the Chemical Lecture Room of the Ohio Mechanics Institute. An address entitled "Chemical Theories" was delivered by Mr. Joseph Ellms.

Reports of the Boston Meeting were made by Prof. H. S. Fry, Dr. E. Reemelin and Dr. Alfred Springer.

ALFRED SMITH, *Recording Secretary.*

WASHINGTON SECTION.

The 195th meeting was held Thursday, January 13, 1910, at 8 P.M., in the Chemical Lecture Room of George Washington University. The following program was presented: "Nitrification in Soils," K. F. Kellerman, E. R. Allen and I. G. McBeth (B. P. I.). "Availability of Iodophenin in the Separation of Acetanilid and Acetphenetidin," W. O. Emery (Bur. Chem.). "Translocation of Plant Food during Germination of Wheat," J. F. Breazeale (Bur. Chem.).

J. A. LECLERC, *Secretary.*

DECEASED MEMBERS.

John D. Billings, Syracuse, N. Y.
Charles B. Dudley, December 21, 1909, Altoona, Pa.
Ottokar Hofmann, December 24, 1909, Kansas City, Mo.
W. A. Syme, Raleigh, No. Car.

Charles Benjamin Dudley.

In the death of Dr. Charles B. Dudley, which occurred on December 21, 1909, at his home at Altoona, Pa., the result of a brief and unusually severe attack of pneumonia, the *American Chemical Society* has lost one of its most valued members, whether measured by the duration of his connection with the Society, the wisdom and helpfulness of his counsel, or his loyalty to its interests; chemical science has lost one of its most able exponents; and the country a most patriotic and useful citizen.

Dr. Dudley was the son of Daniel and Miranda Bemis Dudley, both of New England origin, and was born at Oxford, N. Y., July 14, 1842. His boyhood appears to have been such as was then typical of the intelligent country lad and was made up mainly of attendance upon the local school and academy, and work upon the farm, with such recreations as village life afforded. He found in this experience incentive for further study, and had commenced his preparation for college when the Civil War broke out, and he determined to enlist in the One Hundred and Fourteenth Regiment of New York Volunteers in 1862. During the period of his enlistment he took part in seven battles and was severely wounded in the leg on September 19, 1864 at Opequan Creek, which resulted in a permanent lameness. During his military service he devoted a portion of his time to study, and on his return to his home in 1865, he renewed his preparation for college at Oxford Academy and Collegiate Institute, subsequently entering and graduating from Yale College with the degree of A. B. in 1871. A year of work upon a newspaper at New Haven was followed by two years of study along chemical lines at the Sheffield Scientific School, and the award of the degree of doctor of philosophy in 1874, and this, in turn, by a year as assistant to Professor George F. Barker in the department of physics of the University of Pennsylvania. A prospective period of service as teacher of science at Riverview Military Academy, Poughkeepsie, N. Y., was interrupted at the end of a month by his acceptance, November 10, 1875, of the position of chemist for the Pennsylvania Railroad Company at Altoona, Pa., a position which (with the title changed to that of chief chemist) he held at the time of his death. He was married on April 17, 1906, to Mary V. Crawford, who survives him.

Dr. Dudley was a charter member of the American Chemical Society, for many years a member of its Council and Board of Directors, and President of the Society from 1896 to 1898. He had been President of the American Society for Testing Materials since 1902 and at the time of his death was also President of the International Association for Testing Materials. He was also President of the Bureau for Safe Transportation of Explosives of the American Railway Association, and a member of a large number of the national societies, including those of civil, mining, mechanical, electrical and sanitary engineering, as well as the Washington Academy of Science, The American Historical Society, The American Philosophical Society, and the Iron and Steel Institute of Great Britain, and other foreign societies. His club membership included the Union League of Philadelphia, The Cosmos Club of Washington, The Chemists' Club and the Engineers' Club of New York.

The mere outline of Dr. Dudley's life and affiliations is itself an index of the catholicity of his interests and the wide range of his activities. During the thirty-four years of his service as chemist of the Pennsylvania Railroad Company he was instrumental in building up their system of tests from its beginning in 1875, when a few hundred dollars' worth of material only was reported upon, to the present elaborate and efficient system of purchase under specification and the series of testing laboratories, not only in chemistry but in allied sciences, which either came under his supervision or for which his advice was often sought. These laboratories now pass upon nearly as many million dollars' worth each year as hundreds of dollars' worth in 1876. The influence of this work upon the interests and welfare of The Pennsylvania Railroad itself, great as it has been, is but a part of the results of Dr. Dudley's life work; for, from this work may be said to have grown the previously unknown but new general practice of formulation of specifications for the purchase and testing of materials, which has been of such incalculable benefit to commercial interests of all kinds. Dr. Dudley's commanding influence was attained in part through his publication of carefully developed analytical procedures in the scientific journals and in the specifications of the Railroad Company; in part, through recognition of his exhaustive and painstaking study of structural materials, notably irons and steels, with reference to durability and possible improvements, the results of which nearly revolutionized railroad construction; but probably mainly through his strong, sane addresses delivered before various scientific organizations, and particularly through his services as president of the American Society for Testing Materials. No one who has heard his noteworthy presidential addresses could doubt that the success of that Society has been very largely due to the energy and enthusiasm which he devoted to it. His election to the presidency of the International Association was a deserved tribute to his efficient service. In considering his successes one should, moreover, not lose sight of the influence of his character, which combined the mind of the thoughtful, careful student, with sound judgment in practical affairs, and a remarkably keen sense of equity, all these traits being further combined with a uniform good nature which went far to enable Dr. Dudley to bring men of initially widely divergent opinions to a common understanding.

Dr. Dudley's life was unique in its breadth of scientific experiences and in the variety of questions upon which it was necessary to express an intelligent opinion and of problems for which a solution was demanded. His pioneer work on irons and steels, which gave him a position of authority with both manufacturers and consumers, and his extended contributions to chemical analysis referred to above are two of the important phases of his scientific achievements. His study of the chemistry and physics of the bronzes and bearing metals resulted more or less directly in the modification of the construction of journals, with a marked increase of bearing surface, which was doubtless a factor in the development of the present high-capacity freight car and probably of other modern forms of rolling stock as well. A careful study of the ventilation of passenger cars, and the ventilation and disinfection of sleeping cars was made under his direction. His widely recognized standing as an authority upon matters relating to the transportation of explosives and other hazardous materials was the outcome of many years of study and experimentation which he himself regarded as a most important part of his scientific work, and his advice regarding these matters was constantly sought.

These are but a very few of the lines along which he thought and worked, which come readily to mind. Of the almost countless individual problems which he met, and often solved, no one could write save Dr. Dudley himself, and it is indeed unfortunate that the exigencies of his busy life prevented him from carrying out his expressed intention to give permanent form to a record of activities which would have possessed much more than ordinary interest and value. But Dr. Dudley was a tireless worker, and was so often called upon to assume new responsibilities that it would not be strange if the load had become heavier than even he could properly hope to carry. He always, however, gave freely of his time, energy, and counsel to worthy causes. His services to this Society are a token of this, and these will be gratefully recalled by many members, especially those familiar with the stressful days of the earlier years of the Society's existence.

His interest in his fellow men is also conspicuously demonstrated in his work for the Altoona Mechanics' Library, which is largely the product of his efforts.

Dr. Dudley's name will stand among American chemists as an example of the scholarly, broad-minded, tireless worker, modest yet courageous and tactful, who contributed to applied chemistry in its largest sense and in a measure which it is yet impossible to estimate. His friends will retain many memories of delightful companionship, quick sympathy with joy or sorrow, helpful counsel in perplexity, and unselfish service in time of need.

H. P. TALBOT.

Issued with the March Number, 1910.

Proceedings.

COUNCIL.

Ex-President Whitney, according to the vote at the Boston meeting, has after consultation with the Executive Committee of the Division of Agricultural and Food Chemistry, appointed H. J. Wheeler, Chairman, J. H. Long, Wm. McPherson, H. C. Sherman, F. T. Shutt, Alfred Springer, A. L. Winton and L. L. Van Slyke a committee to consider the question of the publication of a Journal of Agricultural and Food Chemistry.

President Bancroft has appointed G. C. Stone and H. P. Talbot members of the Committee on Standard Methods of Analysis, of which W. F. Hillebrand is Chairman. CHARLES L. PARSONS, *Secretary.*

MEMBERS ELECTED BETWEEN JANUARY 15TH AND FEBRUARY 15TH.

Abbott, Wm. G., Jr., 54 Park St., Lynn, Mass.
Ackermann, Franz W., 17 Battery Place, New York City.
Ageton, Charles N., Pullman, Wash.
Atkinson, H. V., 55 West 9th Ave., Columbus, Ohio.
Bache-Wiig, Carl, Berlin, N. H.
Baird, R. O., Agric. Exper. Station, Stillwater, Okla.
Balhié, José, Box 935, Habana, Cuba.
Baker, J. A., Indianola, Iowa.
Barston, James M., Jr., 221 South 6th St., Council Bluffs, Iowa.
Batchelder, L. H., 877 Snelling Ave., St. Paul, Minn.
Beckley, Waldron C., 169 Benton St., Hartford, Conn.
Bishop, Earl S., Experiment Station, Lincoln, Nebr.
Blackmer, Fred. L., 32 Orchard St., Jamaica Plain, Boston, Mass.
Bose, Pavitra K., 912 Nevada St., Urbana, Ill.
Bradway, M. R. F., 814 E. Genesse St., Syracuse, N. Y.
Brant, Paul, 5812 Wabash Ave., Chicago, Ill.
Broderson, H. J., Lawrence, Kans.
Brodie, R. K., Corvallis, Oregon.
Brown, David, c/o David Brown & Son, Ltd., Donaghmore, Grt. Britain.
Buckie, Robert H., 19 N. Main St., Mechanicsville, N. Y.
Burdick, Charles F., 1156 23rd St., Des Moines, Iowa.
Burpee, Albert B., Box 316, Orono, Maine.
Butler, Edward C., 85 Tompkins St., Cortland, N. Y.
Butler, Thomas H., c/o Wm. Butler & Co., Ltd., Crews Hole, Bristol, Eng.
Cade, Overton, Jr., Youngsville P. O., La.
Camp, Arthur D., 93 Broad St., Boston, Mass.
Campbell, Charles L., 22 E. Beale St., Wollaston, Mass.
Campbell, James R., Scottdale, Penna.
Carney, Robert J., 720 Whaley Court, Ann Arbor, Mich.
Carver, G. M., c/o The Hampton Co., Easthampton, Mass.

Cederberg, Hilmer, Hagaström, Sweden.
Chase, Henry A., Box 1167, Berlin, N. H.
Colby, George E., Univ. of California, Berkeley, Calif.
Collison, S. E., Univ. of Florida, Gainesville, Fla.
Connolly, Eugene L., Mass. Inst. of Technology, Boston, Mass.
Coon, Joseph L., 675 Greene Ave., Brooklyn, N. Y.
Cooper, William F., 7 Grosvenor Rd., Watford, England.
Corts, F. L., 319 West 134th St., New York City.
Cowan, Roysel J., Nat'l Malleable Castings Co., Toledo, Ohio.
Czapek, Frederick, 11 Weinberggasse 3*a*, Prague, Austria.
Crenshaw, James L., Princeton, N. J.
Crockett, S. D., Jamesville, N. Y.
Crossley, M. L., Brown University, Providence, R. I.
Dalley, Parley, Cedar City, Utah.
Das, K. C., Box 1244, Stanford University, Calif.
Davidson, Joe V., 1107 N. Eighth St., Terre Haute, Ind.
Davis, John F., 90 West St., c/o Rob't W. Hunt & Co., New York City.
Davis, Nelson C., 69 Southern Ave., Dorchester, Mass.
DeBarr, Edwin, Norman, Okla.
Dellschaft, Frederick H., Winnington, Northwich, Cheshire, Eng.
Dennis, Martin, 859 Summer Ave., Newark, N. J.
Dewar, Alexander H., Linoleum Works, Staines, England.
Dewar, Robert, 553 N. 63rd St., Philadelphia, Pa.
Dewey, Bradley, Vandergrift, Pa.
Dickinson, W. E., Columbia, Tenn.
Dixon, F. E., Heekin Spice Co., Cincinnati, Ohio.
Downing, Fred. P., 826 West Dayton St., Madison, Wisc.
Dumas, H. N., Marietta, Georgia.
Dussans, Thomas H., 1 Cornwall Terrace, London, N. W., England.
Enas, Joseph D., c/o Western Distilleries, Agnew, Calif.
Ferguson, Robert H., 9 North Munn Ave., East Orange, N. J.
Ferreira da Silva, A. J., Academie Polytechnique, Porto, Portugal.
Fiske, Pomeroy, Palmerton, Pa.
Fishburn, H. P., Box 813, Moscow, Idaho.
Fitch, Charles H., 515 West 175th St., New York City.
Ford, T. C., 6319 Ellis Ave., Chicago, Ill.
Fredenburg, Geo. B., Point Richmond, Calif.
Frericks, A. G., 316 W. 2nd St., Mishawaka, Ind.
Garrod, Charles C., Box 596, Hibbing, Minn.
Garroway, John, 58 Buchanan St., Glasgow, Scotland.
Gates, Charles B., 79 Prospect St., Houghton, Mich.
Geromanos, Hercules W., 5 Main St. Park, Malden, Mass.
Glaessner, Arthur, Althanplatz, 6, Wien IX, Austria.
Glycart, C. Karl, University of Idaho, Moscow, Idaho.
Goettsch, Henry Max, 145 W. University Ave., Cincinnati, Ohio.
Goodrich, Charles E., Bureau of Chemistry, Washington, D. C.
Gorham, Josiah, Union Pacific Laby., Omaha, Nebr.
Grant, Ernest H., Chemistry Bldg., O. S. U., Columbus, Ohio.
Gray, Ross H., 8919 Meridian Ave., Cleveland, Ohio.
Green, Henry, College Hill, Easton, Penna.
Groner, O. S., Ottawa, Kans.

Guillaudeu, 116 W. 9th Ave., Columbus, Ohio.
Hadlock, Walter L., 1405 Maiden Lane, Pullman, Wash.
Hansman, Frederick G., 928 North 3rd St., Philadelphia, Pa.
Harder, Oscar E., Norman, Okla.
Harkness, Arthur F., Room 502, State House, Boston, Mass.
Hasegawa, Tetsutaro, care Nikko Electric Copper Refinery, Nikko, Tochigiken, Japan.
Hassan, E. Ashton, 56 Somerset St., Ottawa, Canada.
Heaney, Bernard, 8921 Green Bay Ave., Chicago, Ill.
Heess, J. K., care Carnegie Steel Co., New Castle, Pa.
Hendrix, Byron M., Townshend Hall, O. S. U., Columbus, Ohio.
Herzog, G. K., Massena, N. Y.
Hill, Wm. G., care Amer. Rubber Co., East Cambridge, Mass.
Hine, Thomas B., Stanford University, Calif.
Hollander, Chas. S., 2412 N. Broadway, St. Louis, Mo.
Hornsey, John W., 27 William St., New York City.
Hough, William J., 608 The Nicholas Bldg., Toledo, Ohio.
Hovey, E. A., Cascadilla Park, care C. E. Stevens, Ithaca, N. Y.
Hunt, Charles H., Pullman, Wash.
Iwai, Kyosuke, 1511 East 64th St., Chicago, Ill.
Jackson, Arthur A., 443 East 6th St., Cincinnati, Ohio.
Jackson, Ernest W., Godrevy, Saltburn by Sea, Yorkshire, Eng.
Jameson, Philip E., 1635 N. Sawyer Ave., Chicago, Ill.
Jones, A. Halden, 121 No. Flower St., Los Angeles, Calif.
Jones, Ernest, 914 N. McKinley Ave., Canton, Ohio.
Kaplan, M., 1130 Union Ave., Bronx, New York.
Kellogg, David R., Dept. of Chemistry, O. S. U., Columbus, Ohio.
Klein, A. Fred, 205 Third Ave., New York City.
Lawrence, Wm. A., 11 Vandewater St., New York City.
Levi, Alfred S., Rockaway, New Jersey.
Levinson, Samuel, 161 Tompkins Ave., Brooklyn, N. Y.
Levy, Augustus, 1712–7th Ave., Birmingham, Ala.
Littlefield, R. P., Orono, Maine.
Lorenzi, Jos. de, Jr., 518 Stewart Ave., Ithaca, N. Y.
Lovejoy, Wm. H., 170 Crescent Ave., Louisville, Ky.
Luttgen, Eberhard, Ambler, Pa.
Lyman, J. F., Townshend Hall, O. S. U., Columbus, Ohio.
MacDermid, Kate, 2703 Bloomington Ave., Minneapolis, Minn.
Mansfield, Wm. E., 202 Van Rensselaer St., Syracuse, N. Y.
Marshall, Eli K., Jr., Johns Hopkins University, Baltimore, Md.
Mason, Claude I., Boise, Idaho.
Maxson, Ralph N., 366 Transylvania Park, Lexington, Ky.
McBride, R. C., Youngstown, Ohio.
McCaffery, Richard S., Moscow, Idaho.
McGeorge, Wm., Argentine, Kans.
Menges, Franklin, 233 E. Philadelphia St., York, Pa.
Merrill, J. F., Agr. Exp. Station, Amherst, Mass.
Meyer, E. R., 1139 Michigan St., Toledo, Ohio.
Millberry, Guy S., College of Dentistry, San Francisco, Calif.
Monro, Irwin, W., care W. E. Smith & Co., Ltd., Bangalore, India.
Montgomery, G. C., 1623 Manhattan Bldg., Chicago, Ill.

Nachf, Ottmar S., care Stobbe, Dultz & Co., Munchen, Germany.
Newell, Morgan C., Conneaut Lamp Works, Conneaut, Ohio.
Niditch, Isadore, 38 McClellan St., Dorchester, Mass.
Northcote, R. S., 64 Admiral Road, Toronto, Canada.
Nye, Lillian L., 1514–6th St., S. E., Minneapolis, Minn.
O'Brian, L. Étienne, 225 East Huron St., Chicago, Ill.
Ochs, Eric J., Siegfried, Pa.
Olmsted, Frederic A., 93 Broad St., Boston, Mass.
Overhuls, Paul L., Box 596, Hibbing, Minn.
Palmer, Erik S., 6 Grant Ave., Livingston Manor, New Brunswick, N. J.
Palmer, Thomas Chalkley, American Dyewood Co., Chester, Pa.
Papazoni, Charles F., care Jefferson Powder Mfg. Co., Birmingham, Ala.
Parkinson, J. C., Massena, N. Y.
Paterson, Alice G., Pullman, Wash.
Pelzer, Joseph, Laubenheim (Rhein), Germany.
Persons, Ashton C., Willimantic, Conn.
Petessen, E. H., 6151 Kimbark Ave., Chicago, Ill.
Pitcairn, Robert F., Barclay Bldg., Greensburg, Pa.
Plancher, Giuseppe, Via Corte d'Appello 15, Parma, Italy.
Pratt, Wm. H., 201 Dryden Road, Ithaca, N. Y.
Prentiss, Daniel Webster, 1213 M. St., N. W., Washington, D. C.
Punnett, Milton B., Pittsford, Monroe Co., N. Y.
Quayle, Wm. O., Pompton Lakes, New Jersey.
Quinlan, Frank J., 188 Broadway, Somerville, Mass.
Rabak, Frank, Bureau of Plant Industry, Washington, D. C.
Randall, Chester, J., 248 Ash St., Waltham, Mass.
Rather, J. B., Experiment Station, College Station, Texas.
Ray, Burton J., Raleigh, No. Car.
Rentschler, M. J., 416 West 23rd St., New York City.
Richardson, Frederic Wm., County Analyst's Office, Bradford, Yorks, England.
Rosenheim, Arthur, Alsenstr. 3, Berlin, N. W. 40, Germany.
Rosenstein, Ludwig, 7 Concord Square, Boston, Mass.
Ross, Elbert, Lafayette College, Easton, Penna.
Russ, Donald E., Oil City, Pa.
Ruston, Percy W., care A. S. Watson & Co., Manila, P. I.
Ryan, Francis C., Grasselli, Indiana.
Samuel, William P., 613 Stevenson St., So. Sharon, Pa.
Scales, Freeman M., 147 Roberta Ave., Louisville, Ky.
Schlesinger, Mildred D., 9 Tower Place, Yonkers, N. Y.
Schlichte, Anton A., 1021 East Huron St., Ann Arbor, Mich.
Schneide, Benjamin B., Pullman, Wash.
Schoenfeld, George J., New York University, University Heights, New York City.
Schuele, Chas. H., Box 387, Pullman, Wash.
Schuette, Henry A., 424 Lake St., Madison, Wisc.
Sen, Kaviraj Nagendra Nath, 18–1 Lower Chitpur Road, Calcutta, India.
Shipley, John W., 12 Oxford St., Cambridge, Mass.

Shippee, Allen E., 478 Columbus Ave., East Greenwich, R. I.
Shuttleworth, Edward B., 220 Sherbourne St., Toronto, Can.
Sierp, H., St. Xavier's College, Bombay, India.
Simon, H., Kgl. Technischen Hochschule zu Berlin, Charlottenburg, 2, Germany.
Sircar, Anath B., Muzaffarpur, India.
Slattery, Thomas W., 4 Middle Converse Hall, Burlington, Vt.
Smith, Claude A., Chamber of Commerce, Atlanta, Ga.
Smith, Edward C., 1129 Birchard Ave., Fremont, Ohio.
Smith, Irving W., 420 East 25th St., Manhattan, New York.
Smith, Philip H., 102 Main St., Amherst, Mass.
Smith, Thur, 254 Boyd Ave., Baton Rouge, La
Sohlman, Ragnar, Bofors, Sweden.
Spence, George K., Johnsonburg, Pa.
Stephenson, J. N., Lawrenceville, N. J.
Szarvasy, Emeric C., University of Technical Science, Budapest, Hungary.
Talbot, Charles Wm., 507 Monroe St., Pullman, Wash.
Tannehill, Lee A., Chemist, Hunt's Perfect Baking Powder Co., Minneapolis, Minn.
Thayer, Allan C., 312–16th Ave., S. E., Minneapolis, Minn.
Thompson, Ernest C., 304 State St., Brooklyn, N. Y.
Thorpe, James B., 712 Van Buren St., Gary, Indiana.
Tucker, Frederick H., U. S. Geol. Survey, Washington, D. C.
Tucker, Greenleaf R., Northampton St., Boston, Mass.
Vail, James G., Delaware Ave. and Howell St., Chester, Pa.
Van Brunt, Nelson N., 216 So. Prospect St., Burlington, Vt.
Van Buskirk, L. H., 40 E. Northwood Ave. Columbus, Ohio.
Van Devanter, I. B., 411 College Ave., Ithaca, N. Y.
Viens, Ephraim, cr. Y. M. C. A., Ottawa, Can.
Wahlin, E. G., 1328 Ohio St., Lawrence, Kansas.
Walker, Lester V., 105 Dewitt Place, Ithaca, N. Y.
Walsh, P. H., Box 569, Magog, P. Q., Canada.
Warner, Arthur L. D., Edgewater, N. J.
Warner, C. S., 12 Walnut St., Wyoming, Cincinnati, Ohio.
Watt, Lynn A., 405 E. Green St., Champaign, Ill.
Webster, Benjamin, The Hill, Pottstown, Penna.
Webster, G. E., 40th and Butler Sts., Pittsburg, Pa.
Webster, Magnus H., 282 Albany Ave., Brooklyn, N. Y.
Wemer, H. H., 128 So. Second St., Bangor, Pa.
Whalley, J. J. A. de, 148 Jerningham Road, New Cross, London, S. E., England.
Wilke, Wm., 86 Norwood Ave., Buffalo, N. Y.
Williams, Richard G., care Norton Co., Worcester, Mass.
Willies, Joseph G., 1768 West 8th St., Brooklyn, N. Y.
Wilson, Robert C., Athens, Ga.
Wilson, Thomas J., 302 Mitchell St., Ithaca, N. Y.
Winkler, Hermann, Frankfort a/M, Germany.
Wiswall, Paul M., 11514 Detroit Ave., Cleveland, Ohio.
Witte, John H., Iowa City, Iowa.
Woods, Carl F., 93 Broad St., Boston, Mass.
Zies, Emanuel G., Athol Terrace, Station D., Baltimore, Md.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

PUGET SOUND SECTION.

The fifth meeting of the Section was held at the Butler Hotel Annex, Saturday, December 4th, at 6.30 P.M. After dinner, the following program was enjoyed: "Some Non-Ionic Reactions," by Dr. W. M. Dehn. "The Status of Powdered Coal as a Fuel," by Dwight C. Farnham.

A. JACOBSON, *Secretary*.

CHICAGO SECTION.

The December meeting was held at the Kimball Café, on Friday evening, December 17th. The program for the evening was "The Council on Pharmacy and Chemistry and the Chemical Laboratory of the American Medical Association," by W. A. Puckner, Secretary, Council on Pharmacy and Chemistry, A. M. A.

After the lecture the following officers were elected for 1910: T. J. Bryan, *Chairman*; H. McCormack, *Vice-Chairman*; A. Lowenstein, *Treasurer*; A. L. Nehls, 4652 Malden St., *Secretary*; W. R. Smith, William Brady, J. Stieglitz, *Councilors*; additional member executive committee, I. M. Bregowski.

The January meeting was held January 28th, at the Kimball Café. The usual dinner preceded the meeting.

Mr. Converse, the retiring chairman, offered to present a medal for the best paper delivered before the Chicago Section during each year, the exact conditions of award and design to be left to a committee appointed by the Section. The committee will report at the February meeting.

W. D. Richardson gave a paper on "The Electrolytic Theory of Corrosion and an Amendment Thereto."

Mrs. Wm. Brady read a paper on "The Entertainment of Ladies at the Boston Meeting," which was one of the most enjoyable papers ever presented before the Section. W. R. Smith reported on the Boston meeting.

A. L. NEHLS, *Secretary*.

NORTH CAROLINA SECTION.

The midwinter meeting of the Section was held Friday, January 14th, at 8 P.M., in the Agricultural Building at Raleigh.

Officers for 1910 were elected as follows: *President*, W. M. Allen; *Vice-President*, Daisy B. Allen; *Secretary-Treasurer*, B. J. Ray; *Councilor*, J. E. Mills; *Reporters*, Manlius Orr, Duncan MacRae.

The following program was presented: "Chemistry of Commercial Feeds," by G. M. MacNider. "The Determination of Flaxseed Products by the Specific Gravity Method," by C. H. Herty and E. J. Newell.

"Caffeine in Our Beverages," by E. V. Howell. "A Comparison of the Foster, the Tagliabue and the New York Board of Health Oil Testers," by Manlius Orr. "Application of Physical Chemistry to the Study of the Oleo-Resins," by C. H. Herty. "Bromination of Anthranilic Acid," by A. S. Wheeler and W. M. Oates. "Nature of Attractive Forces," by J. E. Mills. "The Delicacy of the Diphenylamine Test for Nitrates and Nitrites," by W. A. Withers and B. J. Ray. Account of the Boston meeting was given by J. E. Mills.

BURTON J. RAY, *Secretary.*

CORNELL SECTION.

The 58th regular meeting of the Section was held in Morse Hall, Cornell Univ., Friday, January 14, 1910.

The program presented was as follows: "Further Contributions to the Chemistry of the Phenolsulphonic Acid Method for Nitrates," by D. S. Pratt. "Ammonolysis of Hydrazine Sulphate," by T. W. B. Welsh. "Electrolytic Corrosion of Some Metals," by G. R. White. "The Influence of the Basicity of the Soil and of the Growth of Legumes on the Availability of Soil Nitrogen," by Dr. T. L. Lyon. "Report of the Boston Meeting," by Prof. A. W. Browne.

H. W. GILLETT, *Secretary.*

KANSAS CITY SECTION.

The January meeting of the Section was held at the Y. M. C. A. Building, Tenth and Oak St., Kansas City, Saturday evening, January 15th, at 5 o'clock.

The program began with a paper by Mr. Rudolph Hirsch, on the "Food Law and the Jobber." After dinner Prof. H. Louis Jackson read a paper on the "Food Law and the State," followed by a discussion by A. V. H. Mory and Messrs. Bailey, Willard, Sayre and Crumbine.

E A. WHITE, *Secretary.*

UNIVERSITY OF ILLINOIS SECTION.

The regular meeting of the Section was held January 18th at the Chemistry Building, Urbana, Illinois.

The following topics were presented: "Atomic Weight of Phosphorus," by Dr. Grinnell Jones. "Adiabatic Determination of Heat of Combustion," by Dr. R. H. Jesse, Jr.

The February meeting was held Tuesday, February 15th, at 7.30 o'clock, at the Chemistry Building. The following topics were presented: "The Atomic Weight of Tantalum," by Dr. C. W. Balke. "A Measure of Thermodynamic Positivity and Negativity," by C. G. Derick.

L. H. SMITH, *Secretary.*

PITTSBURG SECTION.

The regular meeting of the Section was held in the new Engineering

Building of the University of Pittsburg, on Thursday evening, January 20th.

The program of the evening was: The Boston Meeting—Brief reports on its most interesting features by Messrs. Porter, Handy, Mason, Phillips, Clement, Allen and Chamberlain. "The Manufacture and Analysis of Smokeless Powder"—Mr. C. G. Storm.

The February meeting was held in the assembly room of the Carnegie Technical Schools, on Thursday evening, February 17th.

The following address was given: "Results of Laboratory and Field Inspection of Various Painting Tests," by Henry A. Gardner, Director of the Scientific Section, Paint Manufacturers' Association of the United States.

JOHN A SCHAEFFER, *Secretary.*

PHILADELPHIA SECTION.

The regular meeting of the Section was held at the Engineers' Club, Philadelphia, Thursday evening, January 20th.

The following program was presented:

Report of the Councilors who attended the Boston meeting of the American Chemical Society.

Papers: "The Cause of Color in Plants," by Henrv Kraemer. "The Extraction of Gold from Sea Water," by Arthur W. Comey. "Is There Caramelization in Riva's Test?" by D. W. Horn.

The February meeting was held at the Engineers' Club, Thursday evening, February 17th.

Two papers were presented as follows: "The Application of the Jet in Chemical Processes," by Dr. Oskar Nagel. "The Chemistry of the Tariff of 1909," by C. C. Roberts. The usual informal dinner was served before the meetings.

F E. DODGE, *Secretary.*

RHODE ISLAND SECTION.

The regular meeting of the Section was held January 20th, at the University Club, Providence, and was preceded by the usual informal dinner.

The paper for the evening was by Dr. John E. Bucher, of Brown University, on "The Structure of Retene and Its Relation to Some Natural Resins." Dr. Bucher showed conclusively that the correct structure of retene is 8-methyl-2-isopropylphenanthrene and not the formula ordinarily published in the literature.

ALBERT W CLAFLIN, *Secretary.*

LOUISIANA SECTION.

The thirty-seventh regular meeting of the Section was held January

21st. A very interesting paper was read by L. A. Becnel on "The Causes of Variations in Sugar House Results."

The following officers were elected to serve for the ensuing year: *President,* Dr. Philip Asher; *Vice-President,* Mr. L. A. Becnel; *Secretary-Treasurer,* Mr. George B. Taylor; *Councilor,* Dr. C. E. Coates; *Executive Committee,* Dr. B. P. Caldwell, Mr. F. C. Johnson, Mr. H. Z. E. Perkins.

GEORGE B. TAYLOR, *Secretary.*

NORTHEASTERN SECTION.

The ninety-sixth regular meeting of the Section was held on January 21st, at the Twentieth Century Club, Boston. It was voted that alternate bi-monthly meetings be held jointly with the New England Section of the Society of Chemical Industry.

Professor Louis Derr, of the Massachusetts Institute of Technology, presented a paper entitled "Color Photography at the Present Time." The lecture was profusely illustrated with very beautiful and striking examples of color photography, including some most remarkable results with brilliant micro-photographs.

K. L. MARK, *Secretary.*

UNIVERSITY OF MISSOURI SECTION.

The sixth regular meeting of the Section was held on Friday evening, January 21st. Mr. C. K. Francis delivered the paper of the evening on the "Glycogen Content of Beef Flesh." Mr. E. A. Perkins gave a short note describing an "Apparatus for Measuring the Comparative Hardness of Fat or Similar Substances."

C. ROBERT MOULTON, *Secretary.*

MILWAUKEE SECTION.

The regular meeting of the Section was held at Milwaukee Public Museum, Friday evening, January 28th.

Two papers was presented as follows: "Iron and Steel," by R. S. MacPherran, Chemist, Allis-Chalmers Co. "Lead Smelting," by B. L. Salomon, Asst. Chemist, C. M. & St. P. Ry.

H. M. SOPER, *Secretary.*

CALIFORNIA SECTION.

The forty-ninth regular meeting of the Section was held on Saturday evening, January 29th, in the College Room of the Bismarck Café, San Francisco.

Dr. E. C. Franklin presented a paper on "The Bearing of Recent Work in Radioactivity on the Atomic Theory."

CHARLES ASH, *Secretary.*

LOUISVILLE SECTION.

The February meeting of the Section was held at the Seelbach Hotel on the 7th at 8 P.M. The regular program was changed somewhat by having four short discussions instead of one paper. Much interest was taken by those present.

The following subjects were presented: "Reducing Oils for Paints," by R. C. Lord. "The Detection of Alumina in Water," by W. H. Lovejoy. "The Purchase of Coal on the B. T. U. Basis," by A. M. Breckler. "Gravimetric Determination of Reducing Sugars," by F. F. Hasbrouck. The usual lunch followed in the Rathskellar. F. F. HASBROUCK, *Secretary.*

CINCINNATI SECTION.

The 157th meeting of the Section was held on Wednesday evening, February 9th, in the Ohio Mechanics Institute.

Two addresses were presented: "The Interpretation and Value of Physical and Chemical Tests in the Control of Water Purification Plants," by Mr. Clarence Bahlmann. "The Biological Features of Water Purification at Cincinnati, Ohio," by Mr. L. G. Gedesche.

ALFRED SMITH, *Recording Secretary.*

WASHINGTON SECTION.

The one hundred ninety-sixth meeting, on Thursday, February 10th, 8 P.M., was held at the Public Library Lecture Hall.

The following program was presented: "Solubility of Gold in Nitric Acid," by F. P. Dewey. "The Detection of the Deterioration of Corn with Special Reference to Pellagra," by C. L. Alsberg and O. F. Black (B. P. I.)

Presentation of Notes, Exhibition of Apparatus, etc.

J. A. LECLERC, *Secretary.*

WISCONSIN SECTION.

The regular meeting of the Section was held at Madison on Thursday, February 10th, at 8 P.M., in the Chemistry Building.

Professor J. L. Sammis presented a paper on "The Separation of Curd from Butter Milk," and Dr. S. M. Babcock presented a paper on "The Importance of Metabolic Water in the Development of Living Organisms."

E. V McCOLLUM, *Secretary.*

NEW YORK SECTION.

The fifth regular meeting of the Session of 1909–'10 was held at the Chemists' Club on Friday, February 11th.

The following papers were presented: "Nucleic Acids," by P. A. Levene. "Determination of Sodium Chloride in Milk," by Paul Poetschke. "Some Colloid-chemical Aspects of Digestion, with Ultra-microscopic Observations," Jerome Alexander. "The Fate of Amino Acids in the Organism," by Graham Lusk. C. M. JOYCE, *Secretary.*

SYRACUSE SECTION.

The fifty-sixth meeting was held as a smoker on Friday, February 11th, 8 P.M.

The following program was presented: "The Chemist and the Community," by A. D. Little, reviewed by M. R. Bradway. "The Conference of the Sections," by President H. C. Cooper. "The Chemist's Place in Industry," by A. D. Little, read by Myron Allen.

WM. H. MCLAUCHLAN, *Secretary.*

SECTION OF EASTERN NEW YORK.

The February meeting was held in the Union College Chapel, Schenectady, on Friday evening, February 18th.

The following paper illustrated by lantern slides was presented: "Modern Bacterial Methods of Sewage Treatment," by Prof. L. P. Kinnicutt.

R. C. ROBINSON, *Secretary.*

MINNESOTA LOCAL SECTION.

The regular meeting of the Section was held Friday evening, January 14th, at 8 P.M., in the Chemical Laboratory of the University. An important business meeting to formulate plans for the entertainment of the National Society at its next winter meeting in Minneapolis was followed by a report on meetings of the Council, and of the Industrial and Organic Divisions at Boston, by G. B. Frankforter, and a report on the Inorganic and Physical Division and the Vice-Presidential address by W. H. Hunter.

FRANCIS C. FRARY, *Secretary.*

DECEASED MEMBER.

Dr. August G. Seher, 110 Montclair Ave., Newark, N. J., died October 7, 1909.

Charles Benjamin Dudley.

Obiit December 21, 1909.

Well have you done the labors of a life
Of service for your country and for God,
Whether the paths of flaming fields you trod
In battle for the Nation rent with strife
Where cannon's thunder smothered drum and fife,
Or following the plow across the sod,
Or tarrying where sons of science plod—
A fount of cheer for comrade, friend and wife.
The ripple of your laugh, the clear sweet light
Of those dear eyes forever closed to earth
Shall glad and guide me as I near the night
Now closing on my day of deeds and mirth,
Its glowing glory waxing ever bright
In th'unfathom'd shadows of the second birth.

HARVEY W. WILEY.

San Francisco Meeting.

The Forty-second General Meeting of the American Chemical Society will be held in San Francisco, California, July 12 to 15, 1910.

The California Section is planning to make this meeting one of the most enjoyable ever held, and it is hoped that a large delegation from the East will attend. We shall have advantage of the lowest convention rate ever given, *viz.*, $62.50 from Chicago and return, with return ticket good until October 31st and departure between July 3rd and 8th. A choice of routes will be allowed coming home with $15.00 additional if the Northern Route *via* Portland, Oregon, is chosen. Special rates from the East to Chicago are also expected.

A cordial invitation has been received from the Puget Sound Section for the members to stop at Seattle as the guests of that Section either going to or coming from the San Francisco Meeting. It is hoped that some arrangement to accomplish this can be made.

A special train from Chicago is offered if one hundred tickets are guaranteed in advance. This train will have all the features of the highest class service of the Western roads. Arrangements will be made for stop-overs and sight-seeing en route. If the Southern route is chosen, stops may be made at Colorado Springs, Grand Cañon, one of the Indian Pueblos, etc. If the train goes *via* Salt Lake City, arrangements may be made to visit the large smelters near-by.

Members are urged to communicate with the Secretary at once in regard to their choice of route, and their intention to be present so that plans may be formulated to please all. We feel practically sure of the special train in which all can go together and enjoy one of the finest outings of our lives. To insure its success, however, it is essential that you do your part by informing me at the earliest possible moment of your intention to be with us.

Every comfort will be provided for ladies. *Reservations for the special train will be given precedence in the order of their receipt.*

CHARLES L. PARSONS, *Secretary.*

Proceedings.*

COUNCIL.

MEMBERS ELECTED BETWEEN FEBRUARY 15TH AND MARCH 15TH.

Almy, Charles, Jr., 147 Brattle St., Cambridge, Mass.
Andrews, Arthur B., 32 High St., Auburn, Maine.
Anthony, Stephen, College of Agriculture, St. Anthony Park, Minn.
Baker, R. E., 611 E. Franklin Ave., Minneapolis, Minn.
Barr, Richard S., Mansfield, Ohio.
Bashore, E. G., care of Babcock & Wilcox Co., Bayonne, N. J.
Bates, John S., Hartley Hall, Columbia Univ., New York City.
Berndt, Albert C., 532 Sims Hall, Syracuse, N. Y.
Blackie, Archibald, 223 James St., Winnipeg, Canada.
Boyle, Jas. J., Box 293, Ambridge, Penna.
Brooks, William Conrad, 540 Lincoln St., Bloomington, Ind.
Buchan, Dean W., 257 Byron St., Palo Alto, Calif.
Cameron, Jasper, 2025 Iowa St., Chicago, Ill.
Caskey, Gardner L., care of Navy Dept., Washington, D. C.
Clayton, Robert E., Hanover, Mass.
Corson, Harry P., Durham, New Hampshire.
Edgar, Arthur, 8 St. James Ave , Boston, Mass.
Emery, Albert G., 49 Fenwood Road, Roxbury, Mass.
Faben, Charles R., care of Washington Gas Co., Washington, D. C.
Fegley, John T., 1602 St. Paul St., Baltimore, Md.
Ferriz, Abraham, Dinamita, Durango, Mexico.
Forster, E. L. S., 359 Cooper St., Ottawa, Canada.
Goodwin, J. G., Girard College, Philadelphia, Penna.
Graben, Howard T., 727 E. Congress St., Detroit, Mich.
Graham, H. C., Provincial Lab'y, Edmonton, Alberta, Canada.
Gunning, D. T., 1620 Manhattan Building, Chicago, Ill.
Haines, Drexel W., 77 Van Buren St., Freeport, Ill.
Haskins, Howard D., 1674 E. 93d St., Cleveland, Ohio.
Haynes, Elwood, Kokomo, Ind.
Henry, Arthur G., care of Link Belt Co., Chicago, Ill.
Hicks, John F. G., 517 So. 42d St., Philadelphia, Penna.
Higgins, Harold L., 23 Cumberland St., Boston, Mass.
Holmes, Roy M., 346 Michigan Ave., South Bend, Ind.
Isham, Robert M., 409 E. 14th St., University Place, Nebr.
Jenkins, David E., Cement, Calif.
Jewett, Walter K., University of Nebraska, Lincoln, Nebr.
Keyes, Frederick G., R. I. Hall, Brown Univ., Providence, R. I.
Kubota, Onro, The 7th High School, Kogoshima, Japan.
Larkin, E. H., 109 St. George St., St. Louis, Mo.
Lehmann, Carl, Jarvis St. Collegiate, Toronto, Canada.
Linville, Clarence P., 406 So. Allen St., State College, Penna.
Long, B. E., care of Mercedita Sugar Co., Cabanes, Cuba.
Martin, L. B., 1418 W. St., Washington, D. C.
Oenslager, George, 92 N. Forge St., Akron, Ohio.

Olson, Karl E., 1710 Summit St., Kansas City, Mo.
Osborne, Charles G., 607 Rush St., Chicago, Ill.
Rothwell, T. E., Provincial Assay Office, Belleville, Ont., Canada.
Rouse, B. Irving, 981 Lake Ave., Rochester, N. Y.
Runey, Chas. F., care of Cudahy Packing Co., Kansas City, Kans.
Scott, William C. 420 Tyler St., Sandusky, Ohio.
Sultan, Fred W., 112 N. Second St., St. Louis, Mo.
Thomson, Stuart, 1 State St., Schenectady, N. Y.
Villavecchia, Vittorio, Laboratorio Chimico Centrale, Piazza Mastai, Rome, Italy.
Weed, Robert C., 65 Charles Field St., Providence, R. I.
Werner, A., Chem. Universitäts Laboratorium, Zurich, Switzerland.
Woodrow, John, 84 Harpenden Road, So. Wanstead, Essex, England.
Yard, A. Townsend, 222 Greenwood Ave., Trenton, N. J.
Young, J. Ulric, Tarkio, Mo.
Zieske, Frederick T., 1845 E. 93d St., Chicago, Ill.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

UNIVERSITY OF ILLINOIS SECTION.

The section was fortunate in securing H. S. Miner, chief chemist for the Welsbach Company, for a lecture on the "Application of the Rare Earths to Incandescent Lighting" on Saturday, January 29th. The lecture was well attended and received with great interest. It was illustrated by use of lantern slides and other demonstrations.

The 29th regular meeting of the Section occurred February 9th, at which time the following papers were presented: "The Atomic Weight of Tantalum," by Dr. C. W. Balke. "A Measure of Thermodynamic Negativity and Positivity," by C. G. Derick.

The regular March meeting occurred Tuesday, March 15th, at 7.30 o'clock at the Chemistry Building.

The following papers were presented: "Equilibrium between Amalgam and Amalgam Solutions," by Dr. Geo. McP. Smith. "The Alkylation of Cyanacetic Ether," by Dr. John C. Hessler. "Opalescence and the Function of Boron in the Glaze," by Mr. R. T. Stull.

L. H. SMITH, *Secretary.*

INDIANA SECTION.

The following papers were read at the meeting of the Section, Friday evening, January 14th, at 7.15 P.M.: "A Simple Method for Determining the Relative Strength of Acids and the Relative Strength of Bases," by W. M. Blanchard, DePauw University. "Some Problems in Iron Analysis," by H. A. Schwartz, Indianapolis.

Supper preceded the meeting.

H. S. Miner, chief chemist of the Welsbach Company, addressed the

Section on "The Rare Earths and Their Use in Incandescent Gas Mantles," at a special meeting held Friday, January 28th, at Shortridge High School.

The following papers were presented at the meeting of the Indiana Section, held at 7.30 o'clock, Friday evening, February 11th, in the office of the State Food and Drug Laboratory: "Laboratory Notes," by Hans A. Duden. "Laboratory Kinks," by R. P. Noble.

On Friday evening, February 18th, the Section gave a dinner at the Columbia Club, Indianapolis. President Stone, of Purdue University, was the speaker.

A. D. THORBURN, *Secretary.*

PUGET SOUND SECTION.

The sixth regular meeting of the Section was held at the "Faculty Club House," University of Washington, Saturday, February 5th, at 8 P.M.

The paper of the evening was on "Conservation and Utilization in the Pacific Northwest," by Dr. H. K. Benson.

The following were elected officers for 1910: *Chairman*, M. J. Falkenburg; *Vice-Chairman*, J. K. Moore; *Councilor*, Dr. H. G. Byers; *Treasurer*, F. F. Flanders; *Secretary*, A. Jacobson.

A special meeting of the Section was held at the Seattle Commercial Club, Thursday evening, Feb. 24th, at 6 o'clock.

After dinner, Dr. R. B. Dole, ass't chemist of The United States Geological Survey, addressed the Section on the "Mineralization of Some American Waters." The address was illustrated with lantern slides.

A. JACOBSON, *Secretary.*

ST. LOUIS SECTION.

The February meeting was held on Monday evening, February 14th, at the Academy of Science Building.

The papers of the evening were: "The Action of Magnesium upon the Vapors of Organic Compounds," by Dr. E. H. Keiser. "The Extraction of Glycerine from Soap Lye," by Mr. Clarence B. Cluff.

R. NORRIS SHREVE, *Secretary.*

LOUISIANA SECTION.

The thirty-eighth regular meeting of the Section was held February 18th. The program consisted of: "Personal Experiences in South African Gold and Diamond Mines," by Thomas Lane Carter, late manager of the French Rand Gold Mine, Johannesburg.

On February 13th, the Section gave a breakfast at La Renaissance des Chenes Verts in honor of the visiting chemists and attorneys in the Bleached Flour Case and other prominent persons.

The thirty-ninth meeting was held at the Directors' Room of the Board of Trade, New Orleans, La., Friday, March 18th, at 8 P.M.

The following papers were presented: "Chemical Examination of

Imported Merchandise," by W. L. Howell. "Some Notes on the Assay of Tincture of Nux Vomica," by G. B. Taylor. GEO. B. TAYLOR, *Secretary*.

KANSAS CITY SECTION.

The February meeting of the Section was held at the new Y. M. C. A. Building, Kansas City, Mo., on Saturday evening, February 19th, at 5 o'clock.

The program began at four o'clock by a visit to the U. S. Assay Office and Laboratories.

At the Y. M. C. A. Building a talk was given by Dr. Charles S. Curtis, U. S. Assayer, Customs Service.

After dinner Dr. Walter M. Cross told the Section about making fertilizer from city garbage.

The March meeting was held at the Chemistry Building, University of Kansas, on Saturday evening, March 12th, at 4 o'clock.

Prof. F. B. Dains, of Washburn College, lectured on "The History of the Development of the Elements."

After dinner Mr. M. Brayton Graff, chemist for the Procter and Gamble Co., spoke on "The Chemical Control of a Soap and Glycerine Factory."

E. A. WHITE, *Secretary*.

CORNELL SECTION.

The February meeting was held Monday, February 21st, in Morse Hall, at 8 P.M.

One hundred members and guests listened to the address, "Problems of the Gas Engineer," by Prof. C. F. Hirshfield.

The March meeting was held in Morse Hall at 8 P.M., Thursday, March 17th, with Dr. J. E. Teeple as speaker on "The Chemical Resources of the United States."

Light refreshments were served as usual. H. W. GILLETT, *Secretary*.

RHODE ISLAND SECTION.

The regular meeting of the Section was held at the University Club, Thursday evening, February 24th.

Dinner was served at 7 o'clock.

Mr. C. E. Swett, of Providence, R. I., then presented the paper for the evening on the subject "Field Notes from the Natural History of Silica."

A special public meeting of the Section, open to ladies and gentlemen, was held in the lecture room of Rhode Island Hall, Brown University, on the evening of Wednesday, March 2nd, at 8 o'clock.

Professor Charles E. Munroe, of Washington, D. C., delivered a stereopticon lecture on "The Testing of Explosives for Use in Coal Mines with Special Reference to the Prevention of Mine Disasters."

ALBERT W. CLAFLIN, *Secretary*.

CHICAGO SECTION.

The February meeting was held at the Kimball Café, on Friday evening, February 25th, at 8.15 o'clock.

The program for the evening was: "Problems of the Linseed Oil Industry," by Otto Eisenschiml, American Linseed Co.

Members of the Section held the usual informal dinner before the meeting.

The Section voted to accept the medal offered by Mr. Converse, and referred the rules for the award of the medal back to the executive committee for further consideration and revision.

A. L. NEHLS, *Secretary*.

NORTHEASTERN SECTION.

The ninety-seventh regular meeting of the Section was held at the Massachusetts Institute of Technology, March 4th.

The following addresses were made: Dr. Daniel F. Comstock, of the Massachusetts Institute of Technology, "Present Conception as to the Constitution of Matter." Mr. M. C. Whitaker, of the Welsbach Co., Gloucester, N. J., "Production of Incandescent Mantles and Chemicals."

KENNETH L. MARK, *Secretary*.

WASHINGTON SECTION.

The one hundred and ninety seventh meeting was held Thursday, March 10th, at 8 P.M., in the Public Library Lecture Hall.

The following program was presented: "The Construction and Equipment of a Chemical Laboratory," by W. D. Bigelow; illustrated with lantern slides; discussion by Chiefs of recently constructed laboratories; presentation of notes, exhibition of apparatus, etc.

J. A. LECLERC, *Secretary*.

SYRACUSE SECTION.

The fifty-seventh meeting was held with the Technology Club at their rooms in the Bastable Block, Friday evening, March 11th.

Dr. A. V. Bleininger, gave an illustrated address on "The Manufacture and Testing of Refractory Material."

WM. H. MCLAUCHLAN, *Secretary*.

SECTION OF EASTERN NEW YORK.

The March meeting of the Section was held in the Electrical Engineering Department of The Russell Sage Laboratory, Rensselaer Polytechnic Institute, Troy, on Friday evening, March 11th, at 8.15 o'clock.

The paper of the evening was: "Wireless Telegraphy and Telephony," by Mr. Wynant J. Williams. The lecture was experimentally illustrated.

R. C. ROBINSON, *Secretary*.

NEW YORK SECTION.

The sixth regular meeting of the session of 1909–'10 was held at the Chemists' Club on March 11th.

The following officers were elected for the session of 1910–'11: *Chairman,* Chas. Baskerville; *Vice-Chairman,* Samuel A. Tucker; *Secretary and Treasurer,* C. M. Joyce; *Executive Committee,* Morris Loeb, G. W. Thompson, J. E. Crane and Arthur E. Hill.

The following papers were read: "The Determination of Copper in Blister and Refined Copper," by Wm. C. Ferguson. "Scrubbing Device for Vacuum System in the Laboratory," by Chas. Baskerville. "Rack for Holding Reagents in Bulk," by J. L. Sporer. "An Improved Ethylene Generator," by V. L. King. "A Constant Temperature Drying Oven and Gas Regulator," by H. T. Beans. "An Automatic Pipette," by S. H. Beard. Description of a Modified Pettersson and Palmquist Apparatus," by C. T. Graham Rogers. "Tests of Iron Wire for Standardization Purposes," by C. H. Stone and C. E. Cheeseman.

C. M. JOYCE, *Secretary.*

CALIFORNIA SECTION.

The fiftieth regular meeting of the Section was held on Saturday evening, March 12th, at 8 o'clock.

An address on "The Electrical Precipitation of Suspended Matter," was given by Dr. F. G. Cottrell, of the University of California.

The usual informal dinner preceded the meeting.

CHARLES ASH, *Secretary.*

CINCINNATI SECTION.

The one hundred and fifty-eighth regular meeting took place Tuesday evening, March 15th, at 8 o'clock, at the Lloyd Library.

Prof. John Uri Lloyd gave the Section a stereopticon evening concerning the Indians of the West, entitled "A Journey through the Navajo and Moqui Indian Countries," with stereopticon views of the Cliff Dwellers' Region.

ALFRED SMITH, *Secretary.*

PHILADELPHIA SECTION

The regular meeting of the Section was held at the Engineers' Club, Philadelphia, Thursday evening, March 17th, at 8 o'clock.

A paper on "The Evidence Obtained during the Past Twelve Years for the Solvate Theory of Solution" was given by Harry C. Jones, Prof. of Physical Chemistry at Johns Hopkins University.

The usual informal dinner was served at the French Club at 6.30 P.M.

F. E. DODGE, *Secretary.*

MINNESOTA SECTION.

The March meeting of the Section was held on Friday evening, March 18th, at 8 P.M. in the Chemical Laboratory of the University of Minnesota. Professor Louis Kahlenberg, of the University of Wisconsin, addressed the Section on "The Chemical Replacement of the Metals by Each Other."

FRANCIS C. FRARY, *Secretary.*

DECEASED MEMBERS.

Reuben Tharp, Jr., San Lorenzo, Calif.

Harold Rollins Wade, Bureau of Chemistry, Washington, D. C.

Oliver Wolcott Gibbs.

When Oliver Wolcott Gibbs died, on December 9th, 1908, American chemists were bereft of one of their leaders, to whom they could look, with affectionate respect, as a pioneer in research, and the true example of the tireless seeker after truth, withal an earnest patriot and a noble gentleman. He was never at the head of a great university laboratory, and the last twenty-five years of his life were spent in retirement from all academic duties; no great body of students are left to mourn the loss of their former teacher. He wrote comparatively few papers of general interest and no books; he shrank instinctively from appearing in the public eye, and the idea of making even an informal after-dinner speech was hateful to him. His austere demeanor and dignified reserve must have always prevented his gaining popularity with the masses, even if his tastes had not led him to prefer scholarly seclusion. To what, then, shall we ascribe the influence which he wielded in the world of chemistry, so that foreign as well as American institutions of learning delighted in showering honors upon him, and considered themselves fortunate if they could obtain his coöperation and advice? Was it not because we all realized that this was a true High-Priest of knowledge, a guardian of the sanctuary, rather than an exploiter of its mysteries; one who could read without an accusing pang, that beautiful distich in which Schiller says of Science:

> Einem ist sie die hohe, die himmlische Goettin, dem Andern
> Eine tuechtige Kuh, die ihn mit Butter versorgt.

Gibbs, a man of modest wants, was probably always possessed of such means that he could restrict himself to the academic side of his profession, and his family traditions and early training would hardly have fitted him for business. I remember conversations with him about the successful careers of his friends, A. W. Hoffman and Joseph Wharton, which made it clear that he would not have attacked a technical problem with any degree of confidence. Perhaps, therefore, a knowledge of his own limitations may have assisted his natural predilections in determining the direction of his work toward pure, one may almost say abstruse, science. But his contemporaries saw a man seeking truth for truth's sake, and they put their trust in this disinterestedness, as well as in his scientific acumen and experimental skill. Justly conscious of his own worth, he was quick to recognize what was meritorious in the work of others, and to applaud, without reserve, the advances along lines quite foreign to his own point of view, while maintaining an almost pathetic veneration for his own great masters, between whom and the present generation he remained one of the last links. Cant, religious, moral or scientific, was abhorent to him, and he could be cruelly caustic in his denunciation of what he deemed charlatancy or insincerity. On the other hand, where he once placed his trust, he left it implicitly, and, when his advice and help were sought, in good faith, he gave of his best. In appearance, and in some respect manners, he resembled James Russell Lowell, to whom I believe he was distantly related. It would have taken considerable boldness to be flippant in his presence, and his students, at all periods of his life, seem to have stood in great awe of him. But he was dearly beloved by friends in and out of academic circles, and he seemed to have the power of impressing his own enthusiasm upon those with whom he collaborated for the public good, as well as for the advancement of science. The Union League and Century Clubs, of New York City, owe their foundation largely to his efforts, just as did the National Academy of Science in Washington; his effectiveness as a member of the U. S. Sanitary Commission, during the Civil War, seemed to have exacted the life-long respect of all his associates.

While, therefore, it was an inestimable gain to the Lawrence Scientific School to secure this master of research, one cannot help wondering whether the narrowness which kept him out of his own alma mater, and forced him to leave the city of his birth, did not curtail some of his most useful powers. Furthermore, the policy which subsequent events have proven thoroughly mistaken, of reducing the Lawrence Scientific School in 1871 from its status as virtually a graduate faculty of natural and exact science, to a shadowy existence as an appendage of Harvard College, deprived Prof. Gibbs of his teaching laboratory, and barred American students of chemistry from working under the direction of a guide who remained for another quarter of a century the master of inorganic research. In fact, during less than eight years of his entire career was he in a position to assign topics for independent research to students in his laboratory, and thus carry out those parallel tests which are the great resource of the modern university professor. Thus it is that the figure of Wolcott Gibbs, even though so recently faded from our eyes, towers in our memory like that of one of the early frontiersmen blazing out new paths in a primeval forest; like the heroes of James Fennimore Cooper, who seek the wilderness from love of nature, not from hatred of man, and who are solitary, not from a saturnine disposition, but from lack of followers willing to forsake easy harvests for the chances of a laborious chase.

But to those who were his immediate contemporaries, Gibbs could not have appeared as a recluse. In the *American Journal of Science*, he was for twenty-two years the eloquent interpreter of the trend of chemistry to workers in other fields of science, and, similarly, the early volumes of the *Berichte der deutschen chemischen Gesellschaft* contain his concise but adequate reports of the achievements of American chemistry. His understanding and sympathy for other branches of exact sciences was great, and, in fact, thermodynamics and optics received much of his attention: he it was, who first appreciated the work of his namesake, J. Willard Gibbs, and insisted on the reward of the Rumford Medal for that treatise on "Equilibrium in Heterogeneous Systems," which became famous twenty years later, when Le Chatelier rediscovered it for the benefit of modern chemists. I could instance, from personal observation, other judgments rendered by him on scientific matter of less moment, in which the clearness of his vision and the thoroughness of his examination proved that no accidental circumstances led him thus to anticipate the trend of physical thought. His contemporaries were stimulated both by the ideas which he freely placed at their disposal, and by the appreciative discrimination which he exercised toward their own scientific efforts.

Born in New York City, on February 21, 1821, as the second son of Col. George and of Laura Gibbs, he was named after his maternal grandfather, Oliver Wolcott, Secretary of the Treasury under Washington and Adams. His boyhood was chiefly spent on his father's farm at Newtown (near what is now Astoria), L. I., and he was educated at the Columbia Grammar School and Columbia College, from which he received the degrees of A.B. in 1841 and A.M. in 1844. He also graduated in medicine from the College of Physicians and Surgeons in 1845, though he never practiced as a physician. His taste for physics and chemistry developed early; he published one or two papers as an undergraduate, worked with Dr. Robert Hare in Philadelphia in 1842, and went abroad in 1845 to specialize in chemistry, under Rammelsberg and Heinrich Rose in Berlin, and under Laurent, Dumas and Regnault in Paris. Returning in 1848, he lectured at Delaware College and the College of Physicians and Surgeons, and was appointed Professor of Physics and Chemistry at the Free Academy of New York City, now the City College, but then practically of high school grade. Here he taught, chiefly by lectures and recitations, until 1863, when he was called to Harvard to fill the Rumford Professorship on the Application of Science to the Useful Arts, recently vacated by Eben Horsford. Attached to this professorship was the Chemical Laboratory of the Lawrence Scientific School, but this was consolidated with the College Laboratory in 1871, under Professor J. P. Cooke, and Professor Gibbs thereafter limited himself to courses in Physical Chemistry, continuing his chemical investigations with the aid of paid assistants. In 1887, he was made Professor Emeritus, and retired to Newport, R. I., where he had always spent his summers on property long in the possession of his family. Here he built a small laboratory, overlooking the beach, in which he continued to work for another decade, until his waning strength warned him to desist. He had lost his dearly loved wife, Josephine Mauran, shortly before his retirement from Cambridge, and he lived very quietly at Newport, attended by a devoted niece, interesting himself chiefly in horticulture as a pastime. He had little taste for the fine arts, but was passionately fond of nature and a friend of all living things. I vividly remember his indignation, one day, when, in the course of a walk, we came across a contractor who was preparing to lop off from a beautiful old tree a great branch that extended into a street through which he wished to move the villa of a summer resident. When the man refused to listen to remonstrances, I was left to guard the tree, while the Doctor set off to find a policeman and finally routed out the Mayor of Newport, with the result that the house had a quarter mile more to travel and the tree was saved.

I have already stated that Gibbs' opportunity to teach advanced chemistry to students was limited to eight years: Prof. F. W. Clarke has given an authoritative account of his teaching at this period, in his beautiful lecture before the Chemical Society of London, (*J. Chem. Soc.*, 95, 1299). My own experience came later, when I fortunately joined the very small class which attended the course in Chemical Physics to which he confined himself after 1871. The formal part of the lesson was frequently dismissed in a few minutes, in which he handed out his full lecture notes, to be copied at home: the remainder of the hour was devoted to experimentation or to purely informal discussion of problems arising out of the general topic. I do not think that the subject was ever treated exhaustively, but we all felt enriched and stimulated when the hour was over. Unfortunately, the course was not correlated to any other work in the University, and I doubt whether, at any one time, more than a dozen undergraduates knew Professor Gibbs by sight.

Privileged, half a dozen years later, to assist him at his private research laboratory, in Newport, I was able to observe more closely his methods of thought and work. He belonged emphatically to what might be termed the Berzelius type of chemist, basing his views upon an intimate knowledge of the reactions of a selected number of elements, and preferring direct deduction from qualitative or quantitative evidence to the experimental substantiation of a hypothesis reached by inductive speculation. His synthetic researches were chiefly carried out in test tubes, without overexact measurements of reacting quantities, of temperature or other conditions. The elaborate search for an *optimum* production of a given compound, so familiar in recent inorganic work, did not appeal to him and he frequently emphasized his desire to point out the directions in which complex compounds should be sought, leaving their careful study to others. Working with the simplest apparatus, almost exclusively in aqueous solutions, he certainly produced an astonishing number of new compounds, whose correlations be was able to point out with considerable verisimilitude. Perhaps he missed a reaction here and there; but few of his critics have been able to state that they failed to find what he did, when they followed his directions closely. As an analyst, he enriched us with some elegant methods, which are not sufficiently emphasized in text books: the determination of manganese as pyrophosphate; the use of mercuric oxide instead of a fixed alkali in precipitating various acids with mercuric nitrate improvements in the estimation of bases as sulphates and oxalates; the detection of cerium by means of bismuth tetroxide or lead peroxide; the use of luteocobalt salts to characterize various acids. The determination of metals by electrolysis, the operation of difficult fusions downward instead of upward, the use of a comparison tube in eudiometric measurements, were all methods first published by him, and many methods developed by others were due to his suggestions. In physics, he early remedied defects in some types of galvanic cell, now obsolete, and he devised improvements of considerable value in the prism spectroscope.

A curious departure from his customary work was his reversion, late in life, to physiological chemistry, when he undertook in 1889 with H. A. Hare and later with E. T. Reichert the systematic study of the action of definitely related organic compounds upon animals. His ideal was the establishment of principles whereby the physiological effect of drugs might be enhanced or modified step by step, so as to produce gradations of physiological effect comparable to the shading of the spectral colors. The experimental work was done by his associates and did not progress far enough to lead to definite conclusions upon this idea.

The name of Gibbs will, however, be chiefly associated with his three great researches on the cobaltammines, the platinum metals and the complex acids. The oxidation of cobalt in ammoniacal solutions had been observed by Gmelin as early as 1822; but F. A. Genth first produced well-defined salts of an ammonia-cobalt base in 1847, publishing his results in 1851, in which latter year papers were published in France by Claudet and by Fremy, who defined four distinct series. Gibbs discovered xanthocobalt in 1852, and thereupon associated himself with Professor Genth, then at the University of Pennsylvania, in a thoroughly systematic study, to which Gibbs seems to have contributed the greater portion of the experimental detail. The results were published by the Smithsonian Institution in December, 1856; but the second series of the work was presented by Gibbs alone to the American Academy of Arts and Sciences in 1874 and 1875. These papers are noteworthy for the thoroughness with which each of the many series was studied, analytically as well as synthetically; he not only showed that the same type of cobaltammine could persist through various combinations with different acids, but also proved that certain acid groups, like NO_2, must be frequently considered an integral part of the base, and that this was notably true of the water, considered by others mere crystal-water, which distinguished the composition of the roseo- from the purpureo-cobalts. His researches were the natural foundation of Werner's theory which has gained general recognition during the past fifteen years.

Analogy to cobaltammines appeared to exist in a compound obtained by Fremy in 1844, by the action of ammonium chloride upon potassium osmiate, and Gibbs proved this, in a brief note published with Genth in 1857, by showing that chlorine could be replaced by other negative radicals without altering the Os: NH_3 ratio. In his final paper, in 1881, he named these compounds the Osmyl-tetramine series. But he was deflected from the continued study of the amines of the platinum group, which he had evidently proposed to himself in 1858, by the interest which the separation and complete characterization of these metals themselves had excited. Working chiefly with refractory California ores, he found it necessary to develop new methods of attack, and his work may well be placed by the side of Claus, Willm and St. Clair-Deville.

Meanwhile, the platin-amines were fully studied by other observers, and Gibbs rather devoted his attention to the behavior of the platinum group to acids. In 1877 he found that the oxides of these metals would unite with the tungstates, to form the salts of complex acids, analogous to the silico-tungstates of Marignac, and this was the starting-point for his great researches on the complex acids, which virtually monopolized the remainder of his experimental activity. Beginning with attempts at systematizing the straggling data on silico-tungstates, phospho-tungstates, etc., recorded by other observers, through the preparation of parallel compounds, he was led to draw one element after another into the complicated molecules that gather around the tungstic or prolyldic nucleus. With a large corps of assistants at his disposal, the work would have assumed gigantic dimensions: but, with a single assistant to carry out the most subtile quantitative separations, his theories must, perforce, await mathematical confirmation, and his cabinet must contain scores of unanalyzed compounds. I believe that he regarded the tungstic acids more or less as the inorganic analogues of hydrocarbons, with certain typical arrangements, into which other groups would enter by direct substitution, largely merging their own identity. Probably, the majority of modern investigators ascribe a more important rôle to these elements of lesser atomic mass; but viewed from the standpoint which I have indicated, the work of Gibbs will show a remarkable consistency, just as his experimental data will, undoubtedly, be confirmed in all essentials by the work of his successors.

And thus the American Chemical Society may well inscribe among its immortals the name of an honorary member, with the words of one of his favorite authors:

> Wer es den Besten seiner Zeit hat gleich gethan
> Der hat gelebt fur alle Zeiten.

MORRIS LOEB.

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

On the evening of February 3, 1910, an informal gathering took place at which there were present among others, most of those to whom had been delegated the task of providing for the creation of an organization for the Eighth International Congress of Applied Chemistry, by the London Congress last June; a representative of the Association of Manufacturing Chemists, the American Chemical Society, the American Electrochemical Society, the Society of Chemical Industry were each also present at this informal meeting.

The consensus of opinion was that the greatest success could be expected only if the most effective system and mode of organization could be had, and if each and every chemist in the United States could be made to feel that he himself, directly or indirectly through his professional, business or educational affiliations, had a personal share of responsibility in the conduct and management of the Congress from its very start and to its very end. This was regarded as the proper and correct guide in proposing any plans or schemes of organization.

The Eighth Congress is to convene in 1912 with Professor Edward W. Morley as Honorary President and Dr. W. H. Nichols as Acting President at a time and place to be determined by the Organization of this Congress. The most important part of the Congress, in fact that by which its value and real success will be measured, is the amount of original matter both scientific and technical, which it will be able to present to its members. To this end, every chemist in America who has or may have any original matter to present to this Congress should begin without delay to prepare such matter, and have it in shape so that it may be presented to the Congress in ample time for proper printing, classification and distribution to members and the technical and scientific press.

The Congress, being held in the United States, will, with a great deal of right, naturally look to a very good showing from the chemists of the United States, and every chemist in this country, which is to be host to our foreign colleagues, should constitute himself a committee of one to get from himself, or from his friends as much scientifically or technically valuable material as possible so that the proceedings and publications of the Eighth Congress may correctly reflect the true mental attitude of the chemists of the United States towards their profession, both as a pure science and as a part of the industrial activities of this country.

It is the hope that the Program Committee will be able to begin its activities effectively before the close of 1910, but in the meantime it behooves every chemist in the United States actively and energetically to consider how and in what way he can best contribute to the success of this Congress, and particularly in the direction of papers and communications to the Congress embodying the advance in this field since June, 1909, the date of the last Congress.

At a meeting to be held in April or May, 1910, by those charged with the duty of providing suitable organization for the Eighth Congress, some definite action as to such organization may be looked for. Those who have that responsibility are making every effort to get as many suggestions as to divisions of organization, mode of organizing and membership of the organization as possible. Every one interested in having this organization on as broad foundation as possible is earnestly invited to present any suggestions that may be helpful in that direction, in writing by the middle of April, 1910, so that all these suggestions may be properly classified and collated and put in condition for most thorough consideration before the meeting above referred to actually takes place. Such communications may be addressed to the temporary secretary, Dr. B. C. Hesse, 90 William Street, New York City.

NEW EDITION OF GMELIN-KRAUT'S HANDBOOK.

Professor Dr. Franz Peters, Gross-Lichterfelde I, Verl. Wilhelmstrasse 26, writes to the Bureau of Standards that he has assumed the editorship of Gmelin-Kraut's "Handbook of Chemistry," 7th edition, since the death of Professor Friedheim, and is arranging for an 8th edition. In order to add to the value of these publications he desires to cover the American field fully and would therefore like to have access to original publications in chemistry and physics. He expresses the wish also to receive copies of all dissertations, relating to inorganic chemistry, of the universities of the United States. This request is made public for the information of authors of dissertations as well as the heads of faculties of chemistry.

Proceedings.

COUNCIL.

By letter ballot sent to the Council on March 4th, the Council voted unanimously that the Secretary be directed to send to the treasurer of the committee in charge of the erection of a monument to Marcelin Berthelot the funds collected by the circulation of a subscription paper at the recent General Meeting of the Society. The amount collected from individuals, amounting to $131.50, has been duly forwarded

In the same communication to the Council the following statement and motion was put and the motion was carried with only two dissenting votes.

"Last fall the Secretary wrote to the head of the chemical department in each of our prominent educational institutions asking him for a list of his alumni engaged in chemical work. This list was then checked off and he was asked to send a letter to each non-member of the Society, the clerical work and postage being furnished by the Secretary's office. As a result some three hundred new members were secured. An interesting fact developed during this correspondence, *viz.*: that our membership among the chemical alumni of the various institutions varied with the particular institution between ten and ninety per cent. It was also noted that those having the larger percentage were those who now urge their senior students to join us. From this fact and many others, the Secretary was impressed with the idea that the future of our Society, and to a lesser extent its present, depends on early interesting those who are to take our places later, for very few students who interest themselves in the profession at large and gain the habit of having our publications on their desks during their under-graduate life leave us later.

"This matter was presented in the form of a motion to the Council at Boston and was referred by them to a committee consisting of A. A. Noyes, T. W. Richards and H. P. Talbot to carefully consider its advisability and legality under our Constitution and By-laws and the requirements of the Post Office Department as to subscribers. This committee have carefully considered the matter and report unanimously the following motion:

"'Under-graduate students may become members of the Society without payment of membership dues during their college course, including the year of their graduation, by making appropriate application and by subscribing to one or more of the Society's publications.'"

MEMBERS ELECTED BETWEEN MARCH 15TH AND APRIL 15TH.

Appell, Geo. M., Hotel Denechaud, New Orleans, La.
Atwood, Edward M., Box 484, Seymour, Conn.
Bandt, Helmuth F., 224 Brooks St., Madison, Wis.
Berry, Jessie V., 1155 Jackson St., Oakland, Calif.
Bose, Amulya C., University of Pittsburgh, Pittsburgh, Penna.
Bosworth, Alfred W., N. Y. Agric. Exper. Station, Geneva, N. Y.

Boyer, G. Hewitt, c/o Continental Portland Cement Co., Jefferson Barracks, Mo.
Bracewell, Geoffrey A., 20 Heaton Grove, Bradford, England.
Brown, Irving C., 533 Sims Hall, Syracuse Univ., Syracuse, N. Y.
Canis, E. N., 2221 Park Ave., Indianapolis, Ind.
Chandler, Louis C., 19th Floor, 1st Nat'l Bank Bldg., Cincinnati, Ohio.
Chapin, Joseph E., 458 Prospect Place, Brooklyn, N. Y.
Clapp, Albert L., 552 Washington St., Braintree, Mass.
de Meeus, E., c/o Michelin Tire Co., Milltown, N. J.
Derby, John H., Jr., 12 Bellaire Drive, Montclair, N. J.
Dobroserdov, Dmitri K., Pokrowskajastreet 14, Kasan, Russia.
Dole, Norman E., 749 Hayes St., San Francisco, Calif.
Evans, Albert W., 5468 Ellis Ave., Chicago, Ill.
Fabinyi, Rudolf, Chemical Inst. of the University of Kolozsvar, Hungary.
Fitch, William W., c/o A. R. Arguelles, Baracoa, Cuba.
Frevert, Gustav E., Moscow, Idaho.
Fulton, Horace M., 1720 Willard St., N. W., Washington, D. C.
Gibbs, Arthur E., Wyandotte, Mich.
Gravelle, Philip O., 183 W. 87th St., New York City.
Hunt, George M., 2323 College Ave., Berkeley, Calif.
Illes, Arpad E., 4494 Forest Park Boulevard, St. Louis, Mo.
Jenckes, Edwin K., 225 Newbury St., Boston, Mass.
Kammerer, Alfred L., Tower Grove and Flad Aves., St. Louis, Mo.
Keeble, Horace, Wereham Hall, Stoke-Ferry, Norfolk, England.
Kendall Mfg. Co., Providence, R. I.
Kitchen, William J., 10-12 Queen St., Melbourne, Australia.
Knowlton, Helen, 27 Central St., Beverly, Mass.
Kressel, Edward C. L., 827 Washington St., Hoboken, N. J.
Leasman, E. L., 901 University Ave., Madison, Wis.
Lehn and Fink, 120 William St., New York City.
MacGregor, H. P., 1907 Division St., Nashville, Tenn.
Marsh, Harry, 430 East A St., Moscow, Idaho.
McDanell, Louise, 100 S. 4th St., Alhambra, Calif.
McElroy, K. P., 197 Pearl St., New York City.
McKesson, Donald, 91 Fulton St., New York City.
Merrell, Lewis C., 502 W. Onondaga St., Syracuse, N. Y.
Mitke, Charles A., 726 Yale Station, New Haven, Conn.
Mukerji, Prafulla C., University of Pittsburgh, Pittsburgh, Penna.
Nicholas, H. E., Eastport, Maine.
Pedersen, Arthur Z., Beach Lane, So. Bensonhurst, Brooklyn, N. Y.
Perkins, H. Z. E., 128 N. Peters St., New Orleans, La.
Platts, Howard C., 38 Sylvan St., Rutherford, N. J.
Putt, Earl B., 711 Tenth Ave., North, Fargo, N. D.
Sarles, Edgar H., 2713 Norwood Ave., Norwood, Ohio.
Saunders, Charles W., 740 Hope St., Shreveport, La.
Scales, Robert R., Greenville, So. Car.
Schmidt, George C., Bureau of Chemistry, Washington, D. C.
Sheridan, A. L., 9240 Manistee Ave., Chicago, Ill.
Shimomura, Kotaro, Shinkanasumaru Kojinguchi Sagaru, Kyoto, Japan.
Sieplein, Otto J., Grove City, Penna.

Smart, Robert, 113 Whiting Bldg., Albuquerque, N. M.
Sprau, R. L., 1108 Logan St., Louisville, Ky.
Steese, Marcus, c/o Ohio Iron-Steel Co., Lowellville, Ohio.
Tarbell, R. F., c/o United Zinc & Chem. Co., Kansas City, Kans.
Tays, James A., c/o City National Bank, El Paso, Texas.
Treadwell, John C., Viesca, Coah., Mexico.
Turley, Everett W., 1038 E. 46th St., Chicago, Ill.
Ullmann, Albert T., Box 30, Chillagoe, Queensland, Australia.
Walker, Seth S., 418 East 2nd St., Mishawaka, Ind.
Walster, Harlow L., College of Agriculture, Madison, Wis.
Weinstock, Sidney, 2224 North Lambert St., Philadelphia, Penna.
Wey, W. G., 6151 Kimbark Ave., Chicago, Ill.
Whitehouse, Joseph, 603 Washington St., Versailles, McKeesport, Penna.
Williams, John M., 218 Water St., Perth Amboy, N. J.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N H.]

INDIANA SECTION.

The following papers were presented at the regular meeting of the Section, held Friday, March 11th, at 7.30 o'clock, in the office of the State Food and Drug Laboratory

"Glass Sands and Ball Clays of Florida," H H. Buckman. "On the Purpose and Methods of the Chemistry Course in the Public High School," F. B. Wade. "The Teaching of Chemistry in the University," J. H. Ransom.

Supper was served at 6 15 o'clock.

A D. THORBURN, *Secretary*

ST. LOUIS SECTION.

The March meeting of the Section was held, in conjunction with the St. Louis Chemical Society, on the evening of March 14th, at the St. Louis Academy of Science Building. The speaker of the evening was Mr. R. F. Weber, who was one of the body of American teachers appointed last year to visit the schools of Germany. Mr. Weber's subjects were: "Chemistry in America and Germany" and "Electrolytic Preparation of Hydrazine." Dr. H. W. Wiley was present and entertained the members by recounting some of his experiences while a student in Germany.

The April meeting was held at the Academy of Science Building, Monday evening, April 11th. The following papers were presented: "Terpineless Extract of Lemon and Analysis Thereof," by Dr. S. H. Baer. "A Rapid Method of Estimating Iron in Iron Ores," by Dr. LeRoy McMaster. "Ozone in Water Treatment" (illustrated with lantern slides, and apparatus for domestic treatment of water with ozone), by Mr. W. F. Monfort.

As is usual the meeting was held in conjunction with the St. Louis Chemical Society.

R. NORRIS SHREVE, *Secretary.*

CHICAGO SECTION.

The March meeting was held at the Kimball Café, on Friday, March 18th, at 8.15 o'clock. The address for the evening was: "The Chemist in a Brass Foundry," by W. M. Corse, Secretary of the American Brass Founders' Association.

After the paper of the evening the Section again took up for discussion the rules for the award of the medal offered by Mr. Converse.

The usual dinner was held before the meeting.

The April meeting, preceded by the usual dinner, was held at the Kimball Café, on Friday evening, April 15th, at 8.15 o'clock, with 120 in attendance. The topic of the evening was: "The Borax Industry, the Mining and Manufacture of Borax and Its Uses," with papers as follows: "The Development of the Borax Industry in California and Nevada, and Sources of Supply in Other Countries," S. T. Mather, Thorkildsen-Mather Co. "Mining and Refining of Borax," F. M. Dupont, Chemist for the Sterling Borax Co. "The Use of Borax in Manufacturing Enameled Sanitary Ware," C. J. Wolff, L. Wolff Manufacturing Co. "The Use of Borax in Manufacturing Enameled Kitchen Ware," Howard Coonley, Coonley Manufacturing Co. The papers were profusely illustrated with specimens of borax ores, borax, and the manufactured products therefrom.

A. L. NEHLS, *Secretary.*

NEBRASKA SECTION.

The fifty-ninth annual meeting of the Section was held in the lecture room of the Chemical Laboratory of the University of Nebraska, Saturday, March 19th, at 8 P.M. The following program was presented: "Present Status of the Bleached Flour Controversy," Dr. F. J. Alway. "Analysis of Soaps," S. H. Ross. "Nitrogen Problems and Dry Farming," R. S. Trumbull. "Determination of Humus," E. K. Files.

O. L. BARNEBEY, *Secretary.*

LOUISVILLE SECTION.

The regular March meeting of the Section was held in Louisville on the 19th. The Louisville members entertained the Lexington, Georgetown and Winchester members at a dinner at noon at the Galt House. The following papers were given: "Antitoxins," Dr. L. A. Brown, of the Food and Drugs Laboratory, Lexington, Ky. "Liquid Mixtures of Constant Boiling Point," Dr. Garnett Ryland, Georgetown, Ky. "Possible Variation in the Composition of Distillers' Dried Grains," Dr. A. M. Peter, Lexington, Ky. "Operation of the Louisville Filter Plant," Mr. W. H. Lovejoy, Chief Chemist of the plant.

Following the papers a trip was made to the Filter Plant where the details of operation were explained.

The April meeting was held at 8 P.M. on the 11th, in Room 700 of the Atherton Building.

Dr. A. M. Peter, Chief Chemist at the Kentucky Agricultural Experiment Station, gave an account of the occurrence of zinc in a large number of Kentucky mineral waters which had been examined at the Station.

Mr. F. M. Scales, of the Louisville Filter Plant, spoke on the "Bacteriological Examination of Water."

The usual light refreshments were served. F F HASBROUCK, *Secretary*

MILWAUKEE SECTION.

The regular meeting of the Section was held at the Trustees' Room, Milwaukee Public Museum, Friday evening, March 25th, at 8 P.M. A paper on "The Methods of Production and Properties of the Chemical Dry Colors" was presented by Mr. C. H. Hall, Supt. of Dry Color Dept., Patton Paint Co. H. M SOPER, *Retiring Secretary.*

RHODE ISLAND SECTION.

The regular meeting of the Section was held at the University Club, Thursday evening, March 31st.

After dinner Professor William H. Kenerson, of the Engineering Department of Brown University, presented the paper of the evening on "Some Problems of the Testing Laboratory." ALBERT W CLAFLIN *Secretary*

NEW YORK SECTION.

The seventh regular meeting of the Section of 1909-'10 was held at the Chemists' Club, on Friday, April 8th.

Dr. F. D. Dodge read a paper entitled "Notes on the Determination of Essential Oils." The remainder of the program consisted of a Symposium on Leather, arranged by Dr. Allen Rogers, which included the following papers: Allen Rogers, "General Outline of the Leather Industry." Alan A. Claflin, "The Process of Bating." John H. Yocum, "Vegetable Tanning Materials." Otto P. Amend, "Recent Advances in Chrome Tannage." F. E. Atteaux, "The Coloring of Leather" (read by Dr. Rogers). Edgar A. Prosser, "Oils Used in the Leather Industry."

C M. JOYCE, *Secretary.*

SECTION OF EASTERN NEW YORK.

The April meeting was held in the Schenectady High School Auditorium, Wednesday evening, April 13th, at 8 o'clock. The paper of the evening was on "Usefulness of Chemistry in Sanitation," by Dr. H. W Wiley, Chief of Bureau of Chemistry, Department of Agriculture, Washington, D. C. At 6 o'clock a subscription dinner in honor of Dr. Wiley was held by the members at the New Vendome Hotel. R. C. ROBINSON, *Secretary.*

CINCINNATI SECTION.

The 159th regular meeting of this Section was held on Wednesday evening, April 13th, at the Lloyd Library. The speaker for the evening was Dr. Alfred Springer, who discussed the following subjects: (*a*) "Salt." (*b*) "Yellow Fever."

ALFRED SMITH, *Recording Secretary.*

WISCONSIN SECTION.

The April meeting of the Section was held at Madison on Wednesday, April 13th, at 8 P.M., in Room 102 of the Chemistry Building. Dr. H. Stanley Bristol, of the Forest Service, U. S. Department of Agriculture, presented a paper on "Some Chemical Problems of the Forest Products Laboratory."

E V McCOLLUM, *Secretary.*

WASHINGTON SECTION.

The 198th meeting and annual smoker was held Thursday evening, April 14th, at 8 P.M., at Fritz Reuter's.

The Smoker began with a beefsteak dinner at 6.30. The regular meeting was called to order at the same place at 8 o'clock and the following program presented: Reid Hunt, "The Effect of Drugs and Diet upon the Thyroid." B. Herstein and Lyman F. Kebler, "Contribution to the Knowledge of Phosphoric Acids." H. C. Fuller, "Separation and Determination of Cocaine and of Atropine from Strychnine."

J A. LE CLERC, *Secretary.*

LOUISIANA SECTION.

The fortieth meeting was held at the Directors' Room of the Board of Trade, New Orleans, Friday, April 15th, at 8.00 P.M. The paper of the evening was "Food in Light of Modern Chemistry," by Dr. Gustav Mann.

GEO B. TAYLOR, *Secretary*

MINNESOTA SECTION.

The twenty-fifth regular meeting of the Section was held Friday evening, April 15th, in the Ohemical Laboratory of the University of Minnesota, with program as follows: "A Correction in the Beckmann Thermometer Due to the Hydrostatic Pressure of the Mercury Column," Prof. Ira H. Derby. "Comparison of Rapid Electroanalytical Methods: Part 1, The Determination of Copper," Francis C. Frary and Andrew P. Peterson.

FRANCIS C. FRARY, *Secretary*

DECEASED MEMBER.

Henry A. Torrey, Harvard University, Cambridge, Mass., March 26, 1910.

Issued with the June Number, 1910.

Proceedings.

COUNCIL.

MEMBERS ELECTED BETWEEN APRIL 15TH AND MAY 15TH.

Adams, Elliot Q., Res. Lab'y, Gen. Electric Co., Schenectady, N. Y.
American Vanadium Co., Pittsburg, Penna.
Ames, W. B. V., 151 Wabash Ave., Chicago, Ill.
Bailey, Clyde H., Agricultural College, Fargo, N. D.
Blauer, I. Theodore, 317 E. 90th St., New York City
Brown, Chas. Wm., 11 W. Michigan St., Chicago, Ill.
Cheney, Gough L., Mt. Pleasant, Iowa
Cooper, J. D., 2408 Longest Ave., Louisville, Ky.
Davis, Eugene R., 149 Rector St., Perth Amboy, N. J.
Dennis, Arthur C., Deerwood, Minn.
Edeler, A., c/o Proctor & Gamble Co., Kansas City, Kans.
Elley, Harold W., Sta. A, Chem. Bldg., Lincoln, Nebr.
Elmer, James M., Tuolumne, Calif.
Enoch Morgan's Sons Co., 439 West St., New York City.
Fairhall, Lawrence T., Danville, Ill.
Forst, Leo B., 1529 Tea St., Washington, D. C.
Garland, Charles S., 18, Derwent Grove, E. Dulwich, London, S. E., Eng.
Graham, Alexander E., Agric. Bldg., Univ. of Calif., Berkeley, Calif.
Guhlmann, Charles F., Grantwood, N. J.
Hadank, Erich, 523 River St., Hoboken, N. J.
Harms, Herman, 48 S. Main St., Salt Lake City, Utah.
Haskell, William O., Orono, Maine
Herstein, Bernard, 1744 Willard Ave., Washington, D. C.
Hess, J. Royden, 163 No. Main St., Phillipsburg, N. J.
Heuser, August, 1367 Sunnyside Ave., Chicago, Ill.
Hoyt, Leslie J., Hillsboro, Ohio.
Jaquish, Ben M., 782 East 18th St., New York City
Kennedy, Miles Bryce, Univ. of Nevada, Reno, Nevada.
Kennedy, Robert P., 119 Stewart Ave., Ithaca, N. Y.
Kudlich, Herman F., Jr., 153 West 21st St., New York City.
Lamont, Charles, 1111 Union Trust Bldg., Detroit, Mich.
Lipstate, W. A., Hartley Hall, Columbia University, New York City.
Lowe, James O., 516 Englewood Ave., Chicago, Ill.
Loy, Sylvester K., Johns Hopkins University, Baltimore, Md.
MacKey, John F., 1428 Tennessee St., Lawrence, Kans.
Marbaker, Edward E., 1615 N. 55th St., Philadelphia, Penna.
Martin, Herbert W., 5225 Woodlawn Ave., Chicago, Ill.
Mason, Stephen N., Ayer Mills, Lawrence, Mass.
McAllister, H. T., $1002^{1}/_{2}$ California Ave., Urbana, Ill.
Mitchell, Thomas A., 79 Elm St., North Woburn, Mass.
Monro, Claxton, 16 Elm St., North Andover, Mass.
Murray, W. S., Lock Box 873, Hamilton, N. Y.
Patton, Walter D., Memorial University, Mason City, Iowa.
Peterson, Leo, Box 331, Emporium, Penna.

Phillips, Percy P., Rurki, United Provinces, India.
Pollock, Frank S., 237 E. Mauch Chunk St., Tamaqua, Penna.
Pritz, Wesley B., 1852 W. 112th St., Cleveland, Ohio.
Rauchfuss, Arthur A., 526 9th St., Brooklyn, N. Y.
Reid, W. D., 2604 St. Mary's Ave, Omaha, Nebr.
Rice, Edward W., Box 358, Santa Cruz, Calif.
Rogers, Rutherford H., 902 Mahoning Ave., Youngstown, Ohio.
Schoellkopf, Jacob F., Jr., 211 Anderson Place, Buffalo, N. Y.
Shepherd, John H., 1443 E. 66th St., Chicago, Ill.
Southern Cotton Oil Co., 24 Broad St., New York City.
Steffens, J. A., Box 278, Spring Valley, N. Y.
Steinkoenig, L. A., Station and Elliot Aves., Arlington Heights, Ohio.
Trenthardt, Ernest L. P., c/o W. B. Alwood, Charlottesville, Va
Wanner, H. E., Box 137, Annville, Penna.
Winkler, John, 2214 Union St., Berkeley, Calif.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

UNIVERSITY OF MISSOURI SECTION.

The seventh meeting of the University of Missouri Section was held Friday evening, March 4th, at the home of Professor Hermann Schlundt. A supper was given at 6 o'clock in honor of the speaker, C. W. Green, at which a number of invited guests were present. After the supper Professor Green addressed the Section on the "Changes in Chemical Composition of Salmon during the Spawning Season."

The eighth meeting of the Section was held March 18th at 7.30 P.M. Mr. L. D. Haigh gave a review of Lawes and Gilbert's work on "Chemical Composition of Some of the Animals Slaughtered as Human Food," and also of Professor Paul Schweitzer's work at the Missouri Station on the "Flesh of Beef Animals."

The ninth meeting of the Section was held Friday evening, April 1st. Professor Sidney Calvert addressed the Section on "Some New View Points in Organic Chemistry."

The tenth meeting of the Society was held Saturday morning, April 23rd. Mr. H. S. Miner, Chief Chemist of the Welsbach Light Company, gave a very interesting address on the "Chemistry of the Rare Earths, with Special Application to Incandescent Lighting."

The eleventh meeting of the Section was held Friday afternoon, April 29th. Professor Hermann Schlundt gave an address on the "Alpha Particle."

C. ROBERT MOULTON, *Secretary*.

INDIANA SECTION.

The regular meeting was held Friday, April 8th, at the Hotel English. F. R. Eldred read a paper on "Deterioration of Various Drug Extracts." E. G. Eberhardt, who is a delegate to the Pharmacopoeial Convention, presented a paper on "The Coming Revision of the United States Pharmacopoeia." The following delegates to the Convention took part in the discussion: J. R. Francis, A. D. Thorburn, W. H. Foreman and C. R. Schaeffer. "The Pharmacopoeia as a Legal Standard in Municipal and State Work" was discussed by H. E. Barnard.

A. D. THORBURN, *Secretary.*

UNIVERSITY OF ILLINOIS SECTION.

The thirty-first regular meeting of the Section was held April 19th, at the Chemistry Building.

The topic of the evening was "Gas Calorimetry," presented by Professor S. W. Parr. The discussion was made very interesting with exhibits and demonstration of apparatus.

This was the annual meeting of the Section, and officers for the ensuing year were elected as follows: *Chairman*, E. W. Washburn; *Vice-Chairman*, P. B. Hawk; *Councilor*, E. Bartow; *Secretary*, Grinnell Jones; *Treasurer*, C. W. Balke.

The annual reports of the officers showed a flourishing condition of the Section.

L. H. SMITH, *Secretary*

A meeting of the Section was held on Tuesday, May 17th, at 7.30 P.M., in the Chemistry Building.

Professor R. C. Curtiss spoke on (1) "Condensations in the Mesoxalic Ester Series." (2) "The Acid Products of the Action of the Red Oxides of Nitrogen on Malonic Esters." Mr. D. A. MacInnes presented "A Comparative Study of the Freezing Points, Conductivities and Viscosities of Aqueous Solutions of Electrolytes Belonging to the Same Ionic Type but Differing in Degree of Hydration." An exhibition of the apparatus used in the investigation accompanied this paper.

GRINNELL JONES, *Secretary*

PITTSBURGH SECTION.

The April meeting was held in the Engineering Building of the University of Pittsburgh, Thursday evening, April 21st. The following interesting papers were read: "Aluminum in Industrial Engineering," by Mr. Earl Blough, Chief Chemist of the Aluminum Company of America, "Thermochemistry of Explosives," by Dr. W. O. Snelling, Chief in Explosives Laboratory, U. S. Geological Survey, Pittsburgh, Pa.

The regular meeting was held in the Carnegie Technical Schools, on Thursday evening, May 19th.

Program: "The Explosive Power of Coal Dusts; A Method of Testing," Joseph C. W. Fraser, Chemist on Coal Research, U. S. Geological Survey. "The Materials Laboratory of The Public Works Department of Pittsburgh," by M. S. Evans, Chief Chemist.

JOHN A. SCHAEFFER, *Secretary.*

SYRACUSE SECTION.

The fifty-eighth meeting was held at the University Club on April 22nd, at 8.00 P.M. Mr. Clifford Richardson addressed the Section on the subject of "Road-making Material."

WM H MCLAUCHLAN, *Secretary*

KANSAS CITY SECTION.

The Section met at Washburn College, Topeka, on Saturday, April 23rd, at 2 P.M.

After a visit to the College the members listened to the following addresses: "Chemistry Fifty Years Ago at Yale," Dr. J. T. Lovewell. "Some Studies in the Reduction of Aldehydes and Ketones," Prof. J. B. Whelan. "On the Relative Digestibility of Unbleached and Bleached Flour," Prof. J. T. Willard and Prof. C. A. A. Utt. Recess was followed by Dr. Crumbine's address and "Notes on Chemical Topics," by Prof. F. B. Dains.

E. A. WHITE, *Secretary*.

RHODE ISLAND SECTION.

The regular meeting of the Section was held at the University Club, Thursday evening, April 28th.

Dinner was served promptly at 7 o'clock, after which Professor Frederic P. Gorham, of the Biological Department of Brown University, presented the paper of the evening on "Chlorine Disinfection of Water and Sewage."

ALBERT W. CLAFLIN, *Secretary*

NORTHEASTERN SECTION.

The ninety-eighth regular meeting of the Section was held at the Twentieth Century Club, Boston, on April 29th. Prof. Henry Carmichael presented a paper entitled "Electrolysis of Chlorides Theoretically Considered," in which he described the advantages of a partition of asbestos cloth impregnated with Portland cement as a means of separating the electrode products in the electrolysis of brine. Mr. Jasper Whiting, in a paper upon "The Electrolysis of Brine," described in detail his electrolytic cell, which makes use of the formation of sodium amalgam but is not open to many disadvantages possessed by the "Castner Process."

K. L. MARK, *Secretary*

MILWAUKEE SECTION.

The regular meeting of the Section was held April 29th, in the trustees' room in the Milwaukee Public Museum. The program consisted of an illustrated talk on "Opaque White Pigments Used in the Manufacture of Paint," by Frank S. Low, of the Experimental Department of the Patton Paint Co., followed by a general discussion on coal, led by Mr. C. B. Dickie and Mr. G. N. Prentiss.

FRANK S. LOW, *Secretary*.

IOWA SECTION.

The annual meeting was held in the Chemistry Lecture Room of Grinnell College, on Saturday, April 30th, at 9 A.M.

The program was as follows: "Some Suggestions on the Determination of Calcium," George Heise. "The Effect of Continued Grinding on Water of Crystallization," Nicholas Knight. "Laurolene," W. A. Noyes. (As by W. A. Noyes, C G Derrick, and L. P. Kyriakides.) "The Manufacture of Absolute Ether," Launcelot Andrews. "The Modern Manufacture of Portland Cement from the Mechanical and Chemical Standpoint" (illustrated), G. P. Dieckmann. "A New Method for the Determination of Humus," A. A. Wells. "On the Quality of owa Deep Well-Waters," W. S. Hendrickson. "The Efficiency of Land Plaster in Preventing the Loss of Ammonia in Manure," W. W. Scott. Reports.

The following officers were elected for the year 1910–1911: *President*, C. N. Kinney; *Vice-President*, W. J. Karslake; *Secretary*, J. N. Pearce.

J NEWTON PEARCE, *Secretary*

CORNELL SECTION.

A meeting was held in Morse Hall, May 2nd, at 8 P.M.

The paper of the evening was on "Some New Developments in Limnology," by Prof. J. G. Needham.

H W GILLETT, *Secretary*.

NEW YORK SECTION.

The eighth regular meeting of the Section of 1909–'10 was held on May 6th, at the Chemists' Club. Prof. Julius Stieglitz, of the University of Chicago, gave a talk on the "Electrolytic Theory of Oxidation and Reduction," illustrated by numerous lecture table experiments.

Preceding Prof. Stieglitz' address the following papers were read: Harrison E. Patten, "On the Action of Crushed Quartz upon Nitrate Solutions." A. F. Seeker and W. E Mathewson, "Estimation of Iodine in Organic Compounds and in the Presence of Other Halogens" (read in abstract by F. H. Pough). G. D. Beal and M. T. Bogert, "Stilbazoles in the Quinazoline Group."

C. M. JOYCE, *Secretary*

CALIFORNIA SECTION.

The fifty-first regular meeting of the Section was held on Saturday evening, May 7th, at 8 o'clock, at Tait's Cafe.

The paper on "Electro Metallurgy of Iron on the Pacific Coast," was by Mr. G. H. Clevenger, of Stanford University.

The usual informal dinner preceded the meeting.

CHARLES S. ASH, *Secretary*

ST. LOUIS SECTION.

The May meeting was held in connection with the St. Louis Chemical Society, on the evening of the 9th, at the Academy of Science Building.

"The Tin Plague" was discussed by Mr. Leo. R. A. Suppan; and the results of "A Study of Some Methods Used in Oil Analysis" were given by Mr. J. J. Kessler and Miss G. K. Mathiason. In this latter paper the relation of the physical properties of various oil mixtures to the corresponding properties of the constituents was shown by means of numerous tables and curves.

After the meeting the usual informal social gathering was held.

R. NORRIS SHREVE, *Secretary*.

CINCINNATI SECTION.

The 160th regular meeting of the Section was held on Wednesday, May 11th, at the Lloyd Library, at 8 o'clock.

The speaker for the evening was Mr. P. F. Wehmer, Municipal Chemist for the City of Cincinnati, and the subject for discussion "Creosote Wood Block."

ALFRED SMITH, *Secretary*.

WISCONSIN SECTION.

The May meeting of the Section was held at Madison on Wednesday, May 11th, at 8 P.M., in Room 102 of the Chemistry Building.

Dr. J. Howard Mathews presented a paper on "Processes of Color Photography."

E. V. MCCOLLUM, *Secretary*.

WASHINGTON SECTION.

The 199th meeting was held on Thursday, May 12th, at 8 P.M., in the Public Library Lecture Hall.

The following program was presented: "The Exact Determination of Sulphur and of Barium in the Presence of Alkali Salts," I. K. Phelps. "The Determination of Nitrogen in the Feces," I. K. Phelps. "Oil Cement Concrete," A. S. Cushman. "The Complexity of the Humus Extract of Soils," E. C. Shorey. "The Separation and Determination of Cadmium in Presence of Copper," Edwin A. Hill.

J. A LECLERC, *Secretary*.

San Francisco Meeting.

The following divisions will hold meetings in San Francisco: Industrial Chemists and Chemical Engineers, Physical and Inorganic Chemistry, Organic Chemistry, Agricultural and Food Chemistry. The Rubber Section and the Section of Chemical Education will hold no meeting. The Pharmaceutical and Fertilizer Divisions will be represented and will hold meetings if conditions warrant. Otherwise any papers offered to these divisions will be presented before one of the others. Details as to train, hotel rates, etc., and any additional information received by the secretary before May 25th will be found in the advertising pages of this number.

CHARLES L. PARSONS, *Secretary*.

Proceedings.

COUNCIL.

The following motion of Dr. Morris Loeb has unanimously passed the **Council.**

"Moved, that the Council approve the action of the New York Section **taken at its meeting** on May 6, 1910, looking toward the establishment of **a Museum and** Chemical Loan Collection, and authorize the Section to **undertake** negotiations for the accomplishment of this object, subject, **however, to a review by the Council."** Charles L. Parsons,

Secretary.

Members Elected between May 15th and June 15th.

Barringer, Laurence E., Gen. Electric Co., Schenectady, N. Y.
Bean, M. J., 20 Cross St., Medford, Mass.
Beatty, Cornelius, College Park, Md.
Beringer, George M., Camden, New Jersey.
Billings, E. F., 76 Freeport St., Boston, Mass.
Binswanger, Jacob G., 1619 North 16th St., Philadelphia, Pa.
Blatz, Frederick J., Wilmington, Del.
Booth, Walter F., Chicago Heights, Ill.
Bowers, Paul C , 1419$^1/_2$ Broadway, Nashville, Tenn.
Brown, Thos. R., 709 E. South St., Frankfort, Ind.
Caswell, Robert G., 47 Hope College, Brown Univ., Providence, R. I.
Chamberlain, Paul R., Box 63, Dewey, Okla.
Curtis, Harry A., Univ. of Colorado, Boulder, Colo.
Dashiel, Paul J., U. S. Naval Academy, Annapolis, Md.
Dearborn Drug and Chemical Works, 2005 McCormick Bldg., Chicago, Ill.
Dickerson, Walter H., Muskegon, Mich.
Edgar Zinc Co., 714-717 Security Bldg., St. Louis, Mo.
Ekroth, Clarence V., 450 Franklin Ave., Brooklyn, N. Y.
Elbert, John J., 44 The Fenway, Boston, Mass.
Eysenbach, G. Gifford, 611 No. 10th St., Philadelphia, Pa.
Flint, J. H., 2489 Howard St., San Francisco, Calif.
Forbes, E. B., Ohio Agric. Exper. Station, Wooster, Ohio.
Gray, Harry LeBreton, Eastman Kodak Co., Rochester, N. Y.
Harris, Charles, West Indian Tobacco Co., Port of Spain, Trinidad.
Hartman, Arthur F., Nappanee, Indiana.
Heilman, Chas. G., 724-3rd St , Catasauqua, Pa.
Hofmann, Lothar, 2205 S. Broadway, Fort Wayne, Ind.
Holman, Ernest C., 3104 Fox St., Chicago, Ill.
Jameson, Miss Eloise, Corona, Calif.
Kendall, George R., 530 Cambie St., Vancouver, B. C.
Klepetko, Frank, 42 Broadway, New York City.
Laird, Joseph Stanley, Caledonia, Ont., Canada.
Lawrence, James C., Kappa Sigma House, Columbia, Mo.
Lawton, Stanley H., President's Hill, Quincy, Mass.

Lothrop, George Van Ness, 440 Jefferson Ave., Detroit, Mich.
Lunt, George, 115 W. 183rd St., New York City.
Macfarlane, Wallace, 25 S. St., Salt Lake City, Utah.
Madge, Norman G., 11 Vandewater St., New York City.
Mautner, L. A., 917 West Green St., Urbana, Ill.
Paine, Harold W., 53 Haskins St., Providence, R. I.
Parsons, L. F., Moscow, Idaho.
Perdue, Wm. L., Princeton, New Jersey.
Perkins, Clement L., Berwick, Maine.
Picard, D. C., Box 885, Atlanta, Ga.
Rankin, Herbert E., 34 South Edwards Hall, Princeton, N. J.
Rhamy, B. W., Fort Wayne, Ind.
Schmidt, Carl L. A., 2338 Roosevelt Ave., Berkeley, Calif.
Schulman, Miss Belle F., 222 So. Second St., Brooklyn, N. Y.
Scofield, Walter W., Jr., Dalton, Mass.
Seaman, Miss Emily C., Teachers' Coll., Columbia Univ., New York City.
Sharples, P. T., West Chester, Pa.
Shuey, Philip MacGregor, Dutton, Fla.
Simon, Clarence, 306 West 99th St., New York City.
Smyth, Chas. H., Princeton, New Jersey.
Spitzer, George, LaFayette, Ind.
Staley, Oscar C., Box 415, Point Richmond, Calif.
Stedman, Chester J., 96 York Square, New Haven, Conn.
Trevithick, Harry P., Refuge Cotton Oil Co., Vicksburg, Miss.
Trewin, H. R., Box 356, Hanover, N. H.
Waldraff, P. H., San Mateo, Calif.
Watson, Warren Neal, 14 Laurel Ave., Auburn, Maine.
Welsbach Company, Gloucester City, New Jersey.
Wheeler, Plumer, Pompton Lakes, New Jersey.
Whipple, Malon, P., Camden, N. J.
Ziegler, Walter W., 363 Madison St., Milwaukee, Wis.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

SECTION OF WESTERN NEW YORK.

The March meeting was held at the University of Buffalo. Mr. G. M. J. MacKay presented a paper on "Cements, Ancient and Modern," describing the recent methods used in making Portland and blast-furnace cinder cement.

The April meeting was held at the Masten Park High School, Buffalo. Prof. E. M. Chamot gave a lecture on "The Microscope in the Chemical Laboratory," illustrated with lantern slides.

The annual election and banquet was held May 20th at Hotel Statler with Vice-President Lidbury in the chair. The following officers for the coming year were elected. *President,* W. H. Watkins; *First Vice-President,* J. I.

Karas; *Second Vice-President*, R. E. Fowler; *Councilor*, F. A. J. Fitzgerald; *Treasurer*, J. Klein; *Secretary*, W. Wallace; *Executive Committee*, F. A. Lidbury, G. H. A. Clowes, A. L. Pouleur.

The presiding officer made an informal address followed by short addresses from each of the elected officers.

The closing hours of the meeting were occupied by listening to remarks of literary interest from many members. Meeting adjourned at 12 P.M.

N. W. SHED, *Retiring Secretary.*

COLUMBUS SECTION.

The regular meeting of the Section was held April 28th in the Chemical Laboratory, Ohio State University. A paper upon "The Recent Developments in the Examination of Proprietary Remedies," dealing vigorously with the ethics of the problems involved, was presented by Prof. C. A. Dye, of the College of Pharmacy, Ohio State University.

Dr. Patterson, editor of Chemical Abstracts, gave an address on the origin and history of our journal, "Chemical Abstracts," as well as the methods of handling the problems involved.

At the previous meeting Dr. John Wilkinson, of the Department of Chemistry, Ohio State University, read a paper on the "Phosphorescence of Some Inorganic Salts," and Dr. J. F. Lyman, Department of Agricultural Chemistry, read a paper on the "Experimental Study of the Metabolism of the Purins in the Mammalian Organisms."

The following officers were elected: *President*, C. W. Foulk; *Vice-President*, A. M. Brumbach; *Secretary-Treasurer*, James R. Withrow, Ohio State University; *Councilor*, Wm. McPherson.

JAMES R. WITHROW, *Secretary.*

UNIVERSITY OF MISSOURI SECTION.

The annual meeting of the Section was held on Friday, May 13th, at 7 P.M. Reports of officers were given and approved. The following officers were then elected for the coming year: *President*, Sidney Calvert; *Vice-President*, R. B. Gibson; *Secretary*, E. E. Morlan; *Treasurer*, Hermann Schlundt; *Councilor*, P. F. Trowbridge.

C. ROBERT MOULTON, *Retiring Secretary*

LOUISVILLE SECTION.

The regular May meeting of the Section was held in Lexington on the 14th, where the Louisville members were the guests of the Lexington members. The visitors were royally treated. The forenoon was spent in automobiling through the blue grass regions and at noon a dinner was served at the Country Club. The party then returned to the Chemical Building of the State University where the meeting was held. Election of the following officers first took place: *President*, R. C. Lord; *First Vice-President*, A. M. Peter; *Second Vice-President*, C. E. Martin; *Secretary*,

F. F. Hasbrouck; *Treasurer*, B. M. Overton; *Councilor*, F. E. Tuttle. Three papers followed: "Colloids," Dr. R. N. Maxson. "Theory of the Continuous Still," A. M. Breckler. "Kentucky Clays," J. S. McHargue. There were about 30 present.

F. F. Hasbrouck, *Secretary*.

PHILADELPHIA SECTION.

The regular May meeting of the Section was held at the Engineers' Club, Thursday evening, May 19th. The annual election of officers resulted as follows: *Chairman*, A. M. Comey; *Vice-Chairman*, C. H. Spayd; *Secretary-Treasurer*, C. S. Brinton; *Executive Committee*, George D. Rosengarten, William H. Bowers, D. W. Fetterolf.

The following papers were presented: "The Chemistry of the Suprarenal Gland," C. E. Vanderkleed. "Analysis of Ground Cloves," Arthur T. Collins.

Clement S. Brinton, *Secretary*.

CHICAGO SECTION.

The May meeting was held in the rooms of the Engineers' Club, on Friday, May 20th, at 8 P.M., with 125 in attendance.

The program for the evening was a "Symposium on Soap," including the following papers: "Special Points to be Considered in the Analysis of Soaps," by Wilson H. Low, Cudahy Packing Co., Omaha, Neb. "The Work of the Glycerine Committee of the American Chemical Society," by A. C. Langmuir, Marx & Ravolle, New York. "Glycerine Analysis," by Robert E. Divine, Detroit, Mich. "The Pears Soap Case: Detection of Volatile Substances in Soaps," by E. M. Slocum, Allen B. Wrisley Co., Chicago. "The Manufacture of Glycerine by the Garrigues Process," by G. A. Moore, Chicago. "Historical Review of Saponification Processes," by W. D. Richardson, Chicago.

The usual informal dinner took place before the meeting.

A L. Nehls, *Secretary*.

LOUISIANA SECTION.

The Section held its forty-first regular meeting in the rooms of the New Orleans Board of Trade, May 20th. Dr. B. P. Caldwell, of Tulane University, gave a lecture on "The Corrosion of Iron."

The 42nd meeting and annual dinner was held Friday, June 17th, 6.30 P.M., at the Old Hickory Restaurant. The topic for discussion was "Chemical Technology in Louisiana."

Geo. B. Taylor, *Secretary*.

KANSAS CITY SECTION.

The Section met at the Y. M. C. A. Building, Kansas City, Mo., on Saturday evening, May 21st at 5 o'clock. The following program was presented: "Chemistry and Cupola Practice," by W. W. Cox, and "Salt Rising Bread," by H. A. Kohman, after which dinner was served.

E. A. White, *Secretary*.

SECTION OF EASTERN NEW YORK.

The May meeting was held in the Union College Chemical Lecture Room, Schenectady, on Wednesday evening, May 25th, at 8 o'clock. A paper on "Accuracy in Certain Difficult Determinations" was presented by Prof. E. W. Morley, followed by refreshments.

The June meeting was held in Little Falls on the afternoon and evening of Saturday, June 11th.

In the afternoon visits were made to Hansen's Laboratory, where Junket tablets are made; to the plant of D. H. Burrell & Company, where milk separators and milking machines are manufactured, to the tannery of the Barnet Leather Company; and to "Overlook," Mr. D. H. Burrell's private residence. After dinner at Hotel Richmond, addresses were given as follows: "The Products of Milk," and the "Junket Tablet," by J. D. Frederiksen, of the Hansen Laboratory; and "Milking Machines and Milk Separators," by Loomis Burrell, of D. H. Burrell & Company.

K C ROBINSON, *Secretary*

RHODE ISLAND SECTION.

The regular meeting of the Section was held at the University Club, Thursday evening, May 26th. Dinner was served at 7 o'clock, following which Dr. Frederick G. Keyes, of Brown University, presented the paper of the evening, "Some Recent Researches in High Vacuum."

ALBERT W. CLAFLIN, *Secretary.*

WISCONSIN SECTION.

A joint meeting of the Milwaukee, Chicago and Wisconsin Section, was held in Milwaukee, May 27 and 28th. The program consisted of a smoker Friday evening, papers by members of the Sections Saturday morning, and a visit to certain technical industries Saturday afternoon.

E. V McCOLLUM, *Secretary.*

NEBRASKA SECTION.

The sixtieth regular meeting of the Section was held at Omaha, Nebraska, Saturday, May 28th. The Section assembled at the Rome Hotel and left by street car at 1.15 P.M. for the Carter White Lead Works in East Omaha, arriving at 2.00 P.M. Leaving there at 3.30 P.M., the members arrived at the Smelter at 4.15 P.M. and left at 5.30 P.M. At 6 P.M. dinner was served at the Rome Hotel. After dinner an address was given by Professor George B. Frankforter, Dean of the School of Chemistry, University of Minnesota, on "Utilization of Waste Wood with Some of its By-Products."

O. L BARNEBEY, *Secretary.*

CORNELL SECTION.

The 62nd regular and 8th annual meeting of the Section was held in Morse Hall, Wednesday, June 1st.

The program consisted of the following reports: "Fractional Crystallization of the Rare Earths," by C. W. Bennett. "Fractionation of the Rare Earths," by H. N. Frear. "Temperature Measurements in the Carborundum Furnace," by H. W. Gillett. "Electrolysis of Certain Liquid Ammonia Solutions," by M. E. Holmes. "Sugar and Alcohol in Apple Waste," by B. J. Lemon. "Sulphated Storage Cells," by G. A. Perley.

The following officers were elected for the ensuing year: *President,* H. W. Redfield; *Vice-President,* F. F. Shetterly; *Secretary-Treasurer,* J. C. Andrews; *Executive Committee,* G. E. F. Lundell, E. F. Hitch, L. J. Cross.

H. W. GILLETT, *Retiring Secretary.*

GEORGIA SECTION.

The Section held its spring meeting in the rooms of the Atlanta Club on the evening of June 4th. Unusual interest was manifested in the business and the papers. It was decided to meet more frequently, the programs subject to the decision of the advisory board. After the meeting the Section adjourned to the Rathskellar to discuss the papers over a Dutch lunch. The papers of the evening were: "The Volumetric Determination of Phosphoric Acid by Precipitation in the Cold," by W. P. Heath. "The Halides of Tantalum," by Walter K. Van Haagen. "Soil Fertility," by F. B. Porter.

J. S. BROGDON, *Secretary.*

NEW YORK SECTION.

The ninth regular meeting of the session of 1909–'10 was held at the Chemists' Club on June 10th.

The following papers were presented: Chas. Baskerville and W. A. Hamor, "The Examination of Ethyl Ether." H. C. Sherman, E. C. Kendall and E. D. Clark, "An Examination of Present Methods of Determining Diastatic Power." E. C. Kendall and H. C. Sherman, "A Study of the Action of Pancreatic Amylase." F. J. Pond, "A Case of Iron Corrosion." Arthur E. Hill, "A Note on the Constancy of the Solubility Product."

C. M. JOYCE, *Secretary.*

DECEASED MEMBERS.

George F. Barker, May 24, 1910, Philadelphia, Pa.
Stanislao Cannizzaro, May 10, 1910, Rome, Italy.
Franklin C. Robinson, May 25, 1910, Brunswick, Maine.

Proceedings.

COUNCIL.

MEMBERS ELECTED BETWEEN JUNE 15TH AND JULY 15TH.

Alanne, W. S., care Sampo Coal Co., Hanna, Carbon Co., Wyo.
Arbuckle Brothers, 71 Water St., New York City.
Arthur D. Little, Inc., 93 Broad St., Boston, Mass.
Baker, H. J. & Bro., 100 William St., New York City.
Bartow, Wm. R., 207 Oneida St., Utica, N. Y.
Benzinger, R., 1219 Chestnut St., Oakland, Cal.
Bernreuter, W., State Water Survey, Urbana, Ill.
Bouton, Craig M., Breckenridge, Colo.
Chemical Products Co., 93 Broad St., Boston, Mass.
Cook, Carl L., 77 Carl St., San Francisco, Cal.
Copes, Louis G., 1216 N. Frazier St., Philadelphia, Pa.
Dick, M. Everett, Holland, Mich.
Fuller, George P., 7 Alfred St., Medford, Mass.
Hammer, R. F., 807 W Church St., Champaign, Ill.
Johnston, W. Armour, Jr., Princes Bay, New York City.
Leeds, John J., care S. & L. Rubber Co., Chester, Pa.
Lester, Charles, 1664 Mance St., Montreal, P. Q., Canada.
Osgood, George D., Hopedale, Mass.
Paisley, John W., 477 West 145th St., New York City.
Perry, Cyrus W., 62 Pine St., Rutland, Vermont.
Peter Cooper's Fertilizer, 111 Broadway, New York City.
Phillips, Alex. W., care Sinnemahoning Powder Mfg. Co., Sinnemahoning, Pa.
Salomon, Ben L., 3020 Mt. Vernon Ave., Milwaukee, Wis.
Stock, G. M., 3610 Clifton Ave., Baltimore, Md.
Stoner, Wm. H., 534 E. Marshall St., Norristown, Pa.
Strauss (Miss) Anna B., 377 Woodlawn Ave., Buffalo, N. Y.
Strosacker, Charles J., Midland, Mich.
Swift, Thos. B., Martinez, Cal.
Vekander, Andrew, Box 547, Petaluma, Cal.

BOARD OF DIRECTORS.

A Directors' meeting was held at the Chemists' Club, New York City, at 8.30 P.M., June 24, 1910, with Directors Bancroft, Hallock, Parker, Love, Little and Parsons present.

It was voted to allow W. D. Richardson sixty dollars per month for clerical expenses while he continues in charge of the advertising and thirty dollars per month thereafter.

It was voted to instruct the Finance Committee to approve such bills as may be necessary to cover the printing of advertisements in the Journal of Industrial and Engineering Chemistry.

It was voted to add one hundred and fifty dollars to Back Number Account for the purpose of reprinting certain numbers of the Journal in

Vols. 3, 4 and 5 that were necessary to complete sets for which orders were already on hand.

In pursuance of a vote of the Council at Boston to the effect that the Directory of the Society be issued as a separate and that the Directors lay down conditions which shall properly safeguard the use of the list from those who wish it for advertising purposes, the Direotors voted as follows:

A. That a single copy of the list may be sent gratuitously to

1. Regular advertisers in our publications but only for their own use.

2. Officers or committees of the Society for Society purposes.

3. Other scientific, benevolent or educational societies in exchange for their own list where same is desired.

B. That on payment of twenty-five cents to cover cost of printing and mailing it may be sent to any member of the Society on signed application therefor stating that the member desires it for his own personal use and that he will not loan or dispose of it to any firm or to any other individual to be used for advertising purposes.

C. That it may be sold by the Secretary to any firm or individual for ten dollars.

It was voted that one thousand dollars be added to that portion of the Budget applying to the printing of Chemical Abstracts.

It was voted that the conditions for free advertisements in the Journal of the American Chemical Society for members seeking employment be changed so as to limit the amount of free insertion to a one-half inch space and to two consecutive insertions but that a third insertion might be allowed upon special request, the change to go into effect on September 1st.

It was voted that the price of Volume 3 of Chemical Abstracts be advanced to ten dollars to members and twelve dollars to non-members of the Society.

The Secretary was instructed to secure sample pages of the Journal of Industrial and Engineering Chemistry printed in 8, 9, and 10 point type for comparison to be submitted to the Directors at a later meeting in order that they might pass intelligently upon the subject referred to them by the Council.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary.*

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

PUGET SOUND SECTION.

The seventh regular meeting was held at the "Faculty Club House," University of Washington, Saturday, March 26th, at 6.30 P.M. Dr. Horace G. Byers addressed the Section on "Some Chemical Curiosities." After the address the Section visited the new chemical laboratories of the University of Washington.

The eighth regular meeting was held at the Engineers' Laboratory, City Hall, Saturday, May 28th, at 8 P.M. Mr. C. J. Moore, Assistant City Engineer, addressed the Section on "Some Notes on the Installation and Operation of the 60-Ton Refuse Destructor at Lake Union."

A. JACOBSEN, *Secretary.*

ST. LOUIS SECTION.

The regular June meeting of the Section was held on the 13th at the St. Louis Academy of Science Building. The subject for the evening was "The National Pure Food Law," which was extensively discussed both from a chemical and from an executive point of view by Mr. D. B. Bisbee, Chief of the Food Inspection Laboratory, St. Louis.

R NORRIS SHREVE, *Secretary.*

SYRACUSE SECTION.

The 59th meeting took place at Frenchman's Island, Oneida Lake, on Saturday afternoon, June 18th, in the following picnic fashion:

2.30 P.M. –Left for Frenchman's Island, *via* South Bay, arriving at 3.45.

4.00 P.M.—Ball game between the Has-Beens of the Halcomb Steel Works and the Never-Wases of the Solvay Process Co.

6.00 P.M.—Supper continuing, until provisions were gone.

7.00 P.M.—Formal installation of officers for ensuing year.

President, E. N. Pattee; *Vice-President*, F. E. Englehart; *Secretary*, W. H. McLauchlan; *Treasurer*, L. M. Fenner; *Nat'l Councilor*, J. D. Pennock.

8.00 P.M.--First detachment leaves for Syracuse.

W H McLAUCHLAN, *Secretary.*

DECEASED MEMBER.

Dr. Wm. H. Seaman, June 10th, Washington, D. C.

Stanislao Cannizzaro.

On May 10, 1910, the American Chemical Society lost by death one of its most distinguished foreign members, Stanislao Cannizzaro. He was born in Palermo, July 13, 1826, where his father was president of the High Court of Chancery. During the revolution of 1848 Cannizzaro, a youth of twenty-two, espoused the cause of the patriots and became a member of the Sicilian Parliament, and an officer of artillery. On the collapse of the Sicilian movement he managed to escape capture and found his way to Marseilles, and thence with the aid of friends to Paris.

He had already been an assistant in the laboratory of Piria, and Cahours now found him a place under Chevreul, where he worked in coöperation with Cloëz. In 1851 he was appointed to a professorship of chemistry at Alexandria in Piedmont; in 1855 he was called to a chair at Genoa, and thence in 1861 to Palermo, where he remained ten years. In 1871 he was transferred to the University of Rome and made a senator of the Kingdom, an appreciation of intellectual merit for which America can offer no equivalent. At Rome the remainder of his life, nearly forty years, was spent, and under his inspiration many of the most famous Italian chemists received their training.

In the great transition from the chemistry of the Berzelian period to the chemistry of to-day, Cannizzaro was perhaps the central figure. During the decade previous to 1858, chemical theory was in almost a state of chaos; nothing seemed to be settled, the noise of inconclusive controversies filled the air. In 1858, however, Cannizzaro published a "Summary of a Course of Chemical Philosophy" which completely changed the aspect of affairs. In this summary the modern system of atomic weights was proposed, which brought the Daltonian constants into harmony with the long neglected law of Avogadro, and the specific heat regularities discovered by Dulong and Petit. A new system of chemical formulae at once replaced the old; the theory of valence assumed shape; the ideas of chemists relative to constitution and structure were clarified. Modern chemistry was born the day that the summary was published, and soon grew into the vast philosophy of our own time. The change that Cannizzaro brought about made all the other changes possible.

Cannizzaro was not a voluminous writer, but his work more than made up in quality what it lacked in bulk. He was essentially an organic chemist. At Paris, with Cloëz, he began the study of the amines, and discovered cyanamide. Later, while at Alexandria, he discovered benzyl alcohol and worked on anisic alcohol with Bertagnini. Practically all of his later studies related to aromatic compounds, and especially to santonin and its derivatives. His active career as an investigator seems to have ended in 1896, when, with Andreocci, he published a research upon the constitution of dimethylnaphthol.

Cannizzaro was the recipient of many honors. He was elected into the great academies of the world, and had honorary membership in the American, British and German Chemical Societies. In 1891 the Royal Society of London gave him its highest recognition, the Copley medal. All these honors were well deserved, for the work of Cannizzaro marked an epoch in the history of chemistry. F. W. CLARKE.

Issued with the September Number, 1910.

Proceedings.

MINUTES OF THE FORTY-SECOND GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The meeting of the American Chemical Society in San Francisco and the sight-seeing and entertainments enjoyed there and en route will always be remembered by those who attended as one of the most pleasant memories of their lives.

The members taking the special train, some 110 in number, gathered at the La Salle Hotel in Chicago on July 4th, where they were entertained at luncheon as the guests of the Chicago Section.

The special train, furnished by the Santa Fe Road, was especially composed of the Pullman Company's finest equipment, electric-lighted throughout, with observation, library and buffet cars.

The first stop was made at Colorado Springs, where most of the members took the trip to Pike's Peak and to the Garden of the Gods, while others contented themselves with the attractions around Manitou and the Cheyenne Canyon.

On the following morning the train stopped for a short period only at Albuquerque and reached Adamana at 1 o'clock, where carriages and wagons were in waiting to take the party to the Petrified Forest, some twelve miles distant. Although the sun shone brightly, no inconvenience was experienced, owing to the altitude and the dryness of the atmosphere, and all were repaid by the wonders awaiting them.

The following afternoon, July 9th, was spent in driving around Redlands and in automobiling through the orchards and palm-grown avenues of Riverside. The party had already been met at the Grand Canyon by Mr. Ralph A. Gould, chairman of the local committee, welcoming them to the State of California on the part of the California Section, and just before reaching Riverside a committee of chemists from Los Angeles met the train and outlined the entertainment to be given by the Los Angeles chemists on the following day.

July 10th was spent in and around Los Angeles as guests of the local chemists, visiting Pasadena, the San Gabriel Mission and Long Beach, and dinner was served at a pleasant resort on the seashore. In the evening the visiting members were entertained with a reception and dinner at the Sierra Madre Club and retired at a late hour to the special train, awaking in the morning at Lang, California. Here the party became the guests of the Sterling Borax Company, visiting their mines on a special train provided for the purpose, and each member received an interesting souvenir of the trip.

That afternoon and evening were spent at Santa Barbara, where a carriage drive was taken and the Santa Barbara Mission visited.

Early the next morning as the party approached Salinas the greatest excitement of the whole trip was furnished by the wrecking of the special train, which ran off the track in rounding a curve, completely destroying the engine and three cars. Fortunately none of the party was seriously hurt, although those in the forward part of the train were severely shaken up. After about three hours' delay, the party proceeded to San José, where they were met by many members of the California Section and were entertained at lunch at the Vendome Hotel. Leaving again for San Francisco, the train was found full of bouquets of sweet peas and baskets of fruit presented to the ladies of the party by the San José Chamber of Commerce.

At 6 o'clock, July 12th, the party arrived in San Francisco and from that time on the hospitality of the California Section was boundless. Every detail had been attended to by the Local Committee. Each member was immediately taken to a taxicab, carried to his hotel, and special vans were waiting for the baggage, which, without any attention on the part of the visiting members, was soon found awaiting them in their rooms. On arrival at the hotel, ladies found bouquets of roses awaiting them.

On Wednesday morning, July 14th, the 42d General Meeting was called to order by President Bancroft in the St. Francis Hotel. After an address of welcome by Arthur Lachman for the California Section, responded to by President Bancroft, the following addresses were delivered in general session.

Positive Photography. Illustrated with lantern slides. W. D. Bancroft.

Liquid Ammonia as a Solvent and the Ammonia System of Acids, Bases and Salts. Edw. C. Franklin.

Chemistry in the Bureau of Standards. W. F. Hillebrand.

The Use of Sodium Benzoate as a Preservative of Food. H. E. Barnard.

At the same time a ladies' reception was held in the parlors of the St. Francis Hotel.

After luncheon the members present and their guests enjoyed an excursion over the Ocean Shore Railroad to Half Moon Bay and Tunitas Glen, returning in time for the smoker held in the Fairmont Hotel, and the ladies' theater party. A hot supper had been promised at the smoker and all who partook of the tamales and heard the Chinese music were ready to acknowledge that the adjective was quite descriptive.

On Thursday morning the meetings of the Divisions were held in the St. Francis Hotel, and many interesting papers were presented. The Symposium on Smelter Smoke before the Industrial Division excited special interest.

After luncheon all attending the meeting enjoyed one of the most pleasant excursions of the trip, made by special train to the top of Mt. Tamalpais and through the Muir Woods, and the members were entertained at a banquet during the evening on the top of the mountain. Several of the members remained all night, coming down the mountain on the following morning in gravity cars. This grove of redwoods, named after John Muir, is probably one of the most beautiful bits of scenery in the immediate vicinity of San Francisco, and the ride to the top of the mountain with the changing interest of foliage and panorama of hill, valley, bay and distant city of San Francisco was appreciated by all.

Friday morning was spent at the University of California in Berkeley, mainly in an examination of the various buildings, laboratories and campus of this beautifully-situated institution.

The party then took a special steamer as the guests of the Selby Smelting and Lead Company, being entertained at luncheon by the Company and afterwards conducted through their plant, where the various processes of lead smelting and the recovery of gold and silver therefrom were explained. One of the chief attractions of this plant was the opportunity given to view the new Cottrell precipitating apparatus installed for the purpose of removing sulphur trioxide and any other solids or liquids present in smelter smoke.

After returning to San Francisco, the evening was spent in a visit to Chinatown, where at 10 o'clock all were entertained at a Chinese collation of tea and sweets served in a Chinese restaurant to music which the Local Committee characterized as sweet.

Saturday morning was devoted to divisional meetings at which the remaining papers on the program were read.

In the afternoon at 2'oclock the members were treated to an automobile ride over Buena Vista Heights, through the Golden Gate Park to the ocean beach and the Cliff House, returning through the Presidio and the residential section of San Francisco.

In the evening the members all assembled for the main banquet of the week in the St Francis Hotel, at which all of the ladies attending were guests. About 250 sat down to the banquet, which will long be remembered by all present.

On July 17th, the party, as the guests of the Italian-Swiss Colony, took a special train to Asti, where an unusually pleasant day was enjoyed in examining the vineyards and wineries of this well-known section. The lunch was served outdoors in unusually attractive pergolas. The party returned to San Francisco early in the evening and were given, almost for the first time, opportunity to sleep.

On the following morning, July 18th, an excursion was taken by steamer up the Sacramento River to Sacramento through the wonderfully fertile fields of the Sacramento Valley, between levees so high that the party was obliged to view the country from the upper deck of the steamer. The general aspect was much like that of portions of Holland. Returning from Sacramento by train, the party reached San Francisco late in the evening, having been royally entertained. Many, however, took train at Sacramento for the north.

On Tuesday, July 19th, a special steamer was provided for those who remained to visit and examine the various points of interest around San Francisco Bay.

Following the meeting in San Francisco, the members returned to their homes by various routes, but some thirty traveled northward by invitation of the Puget Sound Section to visit Seattle and obtain a view of the Northern Pacific Coast scenery. Arriving in Seattle on the morning of the 21st, the party was met by President Falkenburg, of the Puget Sound Section, Horace G. Byers, Councilor of the Section, President Kane, of Washington University, and others, who welcomed them as the guests of the Puget Sound Section.

On arrival the ladies were supplied with bouquets of dahlias, and shortly afterwards all started on an automobile trip which covered all parts of the city, both business and residential, and included the beautiful grounds of Washington University.

At the end of the drive the party was lunched at the Commercial Club, after which they immediately left on a chartered steamer for a trip around Puget Sound. The first stopping-point was the plant of the Pacific Creosoting Company, where the party left the boat and inspected the largest creosoting plant in the world. Returning, a stop was made at the Navy Yard, where battleships and armored cruisers were examined, and then the party proceeded to Tacoma, where a delightful lunch was served under the enormous trees of the Tacoma City Park. By the courtesy of the Board of Park Commissioners, the party was well supplied with roses and given permission to pick all the sweet peas they could carry away.

From Seattle some of the party came east *via* Vancouver and the Canadian Rockies, while others came over the Northern Pacific, visiting the Yellowstone National Park.

Unusual enthusiasm was shown throughout the whole meeting and many new western members were added to the Society, which now has a membership of over five thousand.

290 members and guests registered for the meeting.

120 papers were presented at the meeting embodying new chemical research, many of them reporting very important results.

The programs presented before the various divisional meetings were as follows:

Division of Agricultural and Food Chemistry.

The minutes and program of this Division will be found in the *Journal of Industrial and Engineering Chemistry.*

Division of Industrial Chemists and Chemical Engineers.

A special feature of the program was the Symposium on Smelter Smoke, opened by the following three papers:

The Smoke Problem and the Community. Charles Baskerville.
The Neutralization and Filtration of Smelter Smoke. W. C. Ebaugh.
The Electrical Precipitation of Suspended Matter. F. G. Cottrell.

Details in regard to this symposium and the remainder of the papers presented before the Division will be found in the August number of the *Journal of Industrial and Engineering Chemistry.*

Division of Physical and Inorganic Chemistry.

The following papers were presented to the Division:

Further Studies on the Action of Ammonia upon Ethylphospho-platino chloride. Chas H. Herty and Hamden Hill.

Stratification in Suspensions. F. K. Cameron and E. E. Free.

The Rate of Consolidation of Kaolin Precipitates. F. K. Cameron and E. E. Free.

The Action of Alkalis on Kaolin Suspensions. F. K. Cameron and E E. Free.

The Temperatures of the Carborundum Furnaces. Wilder D. Bancroft.

Salvaging Sulfated Storage Cells Wilder D. Bancroft.

The Silver Coulometer. G. D. Buckner and G. A. Hulett.

Occlusions in Electrolytic Silver. J. S. Laird and G A. Hulett.

An Exact Electrolytic Method for Determining Some Metals W. L. Perdue and G. A. Hulett.

Cadmium Sulphate and the Atomic Weight of Cadmium. W. L. Perdue and G A. Hulett.

Equilibrium in the System KI, I and Aqueous Alcohol. C. L. Parsons and H. P. Corliss.

The Solubility of Barium Nitrate in Solutions of Barium Hydroxide. C. L. Parsons and H. P. Corson.

The Solubility of Strontium Nitrate in Solutions of Strontium Hydroxide. C. L. Parsons and C. L. Perkins.

A Common Thermometric Error in Determining Boiling Points under Reduced Pressure. Alexander Smith.

A Convenient Form of Vapor Density Apparatus. Alan W. C. Menzies.

Basic Nitrates of Yttrium. Chas. James and L. A. Pratt.

The Systems, Lime-Water-Sugar, and Lime-Water-Glycerine at 25° C. F. K. Cameron and H. E. Patten.

Phosphates of Lime, IV. F. K. Cameron and J. M. Bell.

Heats of Neutralization in Non-aqueous Solutions. J. Howard Mathews.

Comparative Analyses of Water from Great Salt Lake. Wallace Macfarlane.

A Suggestion for Instructors in Quantitative Analysis. W. C. Ebaugh.

A Reported Occurrence of Native Iron. W. C. Ebaugh.

Improvements in Molecular Weight Determinations by the Boiling Point Method. L. B. Shipley and J. O. Ziebolz.

The Influence of Organic Liquids upon the Interaction of Hydrogen Sulfide and Sulfur Dioxide. David Klein.

Some Interrelations of the Carbide and Nitride of Magnesium. F. G. Cottrell.

Determination of the Vapor Pressure of Slightly Volatile Solids. H. V. Welch.

Preparation of Pure Anhydrous Ethyl Alcohol. E. C. McKelvy.

Rapid Determination of Mercury, Silver, Bismuth and Copper by means of Stationary Electrodes. R. C. Benner.

The Atomic Weight of Tantalum. Clarence W. Balke.

Concerning the Molecular Weight of Sulphur Vapor. O. F Stafford.

A Rotating Graphite Anode. J. W. Turrentine.

Apparatus for the Determination of Arsenic. Otis D. Swett.

Behavior of Certain Hydrazine Salts in Liquid Ammonia. A W. Browne and A. E. Houlehan.

Electrolysis of Solutions of Potassium Amide and of Ammonium Trinitride in Liquid Ammonia. A. W. Browne and M. E. Holmes.

Electrolytic Corrosion of Various Metallic Anodes in a Solution of Ammonium Trinitride in Liquid-Ammonia. A. W. Browne, M. E. Holmes and J. S. King, Jr.

The Examination of Ethyl Ether: (*a*) A Study of the Tests for Odor, Residue, Acidity and Sulphur Compounds in Ethyl Ether (*b*) The Tests for the Presence of Water and Alcohol in Ethyl Ether. (*c*) On the Changes Occurring in Stored Ether and on the Existence of Ethenol in Ethyl Ether (*d*) The Tests for the Presence of Peroxides and Acetaldehyde in Ethyl Ether. (*e*) On Some New Tests for the Detection of Peroxides in Ethyl Ether. (*f*) The Examination of Ethyl Ether intended for Anesthetic and Reagent Purposes; the Degrees of Purity of American Ethers, and Recommendations for the Standardization of Anesthetic Ether. Charles Baskerville and W. A. Hamor.

Mechanical Stimulus to Crystallization. S. W. Young.

Zinc Ammonium Sulfate. Eloise Jameson.

The Viscosity of Liquid Ammonia, Sulfur Dioxide and Methyl Amine F. F Fitzgerald.

Electrical Conductivity of Solutions in Methyl Amine and Ethyl Amine. F. F Fitzgerald.

Conductivity of Some Solutions in Ammonia Water Mixtures. Wm. H. Sloan.

Cuprous Nitrate. Wm. H. Sloan.

Potassium Ammono-plumbite; Potassium Ammono-cobaltate; Potassium Ammono-nickelate. E. C. Franklin and G. S Bohart.

Chemical Valence and Atomic Charge. Fernando Sanford.

Division of Organic Chemistry.

The Division was presided over by Professor Moses Gomberg acting for President E. C. Franklin, and H. C. Biddle was elected Secretary. A memorial of Dr. H. A. Torrey, a member of the Executive Committee, was read and ordered recorded in the minutes. The following papers were presented to the Division.

1. Action of Acetic Anhydride on *p*-Methoxy Phenyl Propiolic Acid and on Methylene Ether of 3-4 Dihoxy Phenyl Propiolic Acid. Maurice L. Dolt.

2. The Constitution of the Oxonium Salts. M. Gomberg.

3. Action of Amines on Phthalic Acid, VII. Phthalamidic Acids Containing Cl or NO_2 in the Benzene Nucleus. J. Bishop Tingle and S. J. Bates.

4. Camphoroxalic Acid, XIII. Action of Amines on Camphoroxalic Acid. J. Bishop Tingle and S. J. Bates.

5. Stilbazoles in the Quinazoline Group. M. T. Bogert and G. D. Beal.

6. Isocampholactone. W. A. Noyes and A. W. Homberger.

7. Separation of a,a-Dimethyl Adipic Acid into its Optical Isomers and the Synthesis of Laurolene. W. A. Noyes and L. P. Kyriakides.

8. Derivatives of Isocamphoric Acid. W. A. Noyes and Luther Knight.

9. Decomposition of Nitrosophthalalimidine in the Presence of Alcohol. W. A. Noyes and James A. Coss.

10. Conversion of Quinine into Quinotoxime. H. C. Biddle.

11. Metathetical Reactions, Ethyl Thioureas and their Relation to Pseudo-ammonium Bases.

12. The Unsaturated Character of the Resin of *Pinus Sabiniana* Chas. H. Herty and E. N. Tillett.

13. A Study of the Resene of *Pinus Heterophylla.* Chas. H. Herty, W. A. Houck and T. P. Nash.

Numbers 1, 2, 7, 8, 10, 11, 12 and 13 were read and discussed while the others were presented by title only.

Division of Pharmaceutical Chemistry.

The minutes and program of this Division will be found in the *Journal of Industrial and Engineering Chemistry.*

CHARLES L. PARSONS, *Secretary.*

COUNCIL MEETING.

The meeting of the Council was called to order by President Wilder D. Bancroft at 9 o'clock, July 12th, in the Green Room of the St. Francis Hotel, with the following members of the Council present: W. D. Bancroft, C. L. Parsons, C. H. Herty, G. B. Frankforter, A. P. Hallock, F. K. Cameron, F. B. Porter (for W. P. Heath), A. M. Comey (for W. T. Taggart), A. M. Patterson, H. E. Barnard, Felix Lengfeld, H. McCormack (for W. R. Smith), W. L. Dudley, W. F. Hillebrand, G. P. Adamson, W. R. Whitney, C. F. Crowley (for S. Avery), Alex. Smith, W. A. Noyes, H. G. Byers, L. H. Baekeland, F. E. Gallagher (for H. J. Skinner), and M. Gomberg.

Letters from absent members and others, addressed to the Council' were read by the Secretary.

Chairman W. F. Hillebrand, of the Committee on Standard Methods of Analysis, presented a report in regard to the organization of the various committees engaged in standardizing methods of analysis. He stated that owing to the confusion and duplication which had already begun to creep into the work of the General Society and its various Divisions, extensive conferences had been held with the President of the Society, the chairmen and members of the central committee, the chairmen of the Industrial and Fertilizer Divisions and the divisional committees and others and as a result thereof a working scheme had been evolved which was seemingly satisfactory in principle to all who had taken part in the correspondence. He presented full lists of the various committees and showed wherein the duplication and confusion was arising and after careful and thorough discussion by the Council the following resolutions were unanimously adopted for the future government of these committees:

Resolutions Governing Committees of the American Chemical Society, and of Its Divisions, Having to do with the Standardization of Methods of Analysis.

1. Resolved, The name of the Committee on Standard Methods of Analysis (formerly Committee on Uniformity in Technical Analysis) shall be hereafter Supervisory Committee on Standard Methods of Analysis.

The nucleus of the committee shall consist of four members who are not chairmen of subordinate committees. In addition the chairmen of all committees in any way subject to its control shall have the right to deliberate and vote with the committee in all matters concerning the work of their respective committees, and on such additional matters as may be hereinafter specified, and they shall be to such extent members of the committee.

The Supervisory Committee shall remain, as heretofore, under the control of the Council of the Society, but shall be a committee with power.

Nominations to fill vacancies in the nucleus of the committee shall emanate from the full committee and shall be transmitted through the President to the Council for action at a regular meeting, except that an interim appointment may, on request from a majority of the full committee, proceed from the President.

In case of lack of agreement by the committee the President shall himself present nominations to the Council and may, in such case also, make interim appointments on his own responsibility.

2. Resolved, That the functions of this committee shall be as follows:

(*a*) To exercise control of the work of all subordinate committees, to the extent of preventing duplication of work and securing consistency in the form of publication of reports.

(*b*) To examine all reports of divisional or other committees in any way subject to it that are in any way final in the sense of recommending methods or parts of methods for general use. This involves the right to reject entirely such reports or to return them to the committee from which they emanate for such revision as may seem called for. It is assumed that no unduly arbitrary action will be taken in either of these directions, but that any decision rendered will be with a view to uphold the reputation of American chemists and the dignity of the American Chemical Society under whose sponsorship the reports may be published eventually.

3. Resolved, That on passage of the foregoing resolution the existing subcommittees of the central committee that is charged with the investigation of soaps and soap products pass at once, as now constituted, under the control of the Industrial Division, and that the present subcommittee on phosphate rock cease to exist as such, and that its accumulated data be placed by its chairman at the disposal of the corresponding committee of the Fertilizer Division.

4. Resolved, That the foregoing resolution does not abrogate the right of the Supervisory Committee to appoint special subcommittees on lines of work not represented by Divisions of the Society, these subcommittees to be responsible as in the past wholly to the Supervisory Committee.

5. Resolved, That divisional committees having to do with methods of analysis, including that transferred by Resolution 3, shall have full power under the control of their respective Divisions, to initiate and prosecute work, and to publish reports of progress.

Final reports, however, or such as recommend methods or parts of methods, for general use, shall be submitted by the chairman of the divisional committee to the Supervisory Committee for special consideration. Only on approval by this committee, except as hereinafter provided for, may such reports be published, subject to the usual submission to the Board of Editors of one or another of the Society's publications.

If the Supervisory Committee fail within three months to approve or reject a report submitted to it, the President of the Society (acting with the advice of the editors-in-chief of the Society's publications, and of the chairman of the Division concerned) shall be the final judge of its disposition. Acceptance or rejection by the Supervisory Committee within the time limit shall be final.

6. Resolved, That final reports, if published, shall appear as emanating from the particular Division or subcommittee concerned, with the approval of the Supervisory Committee (or of the President of the Society in lieu of approval by the Supervisory Committee as called for in the foregoing resolution), and that they shall be signed by or appear under the name of a majority of the committee under whose supervision they shall have been prepared.

7. Resolved, That the Divisions of the Society may in their judgment appoint either general committees vested with power to appoint and control subcommittees within the Division, or separate coördinate committees for different kinds of work, but in the former case only the chairman of the general committee shall have the restricted membership in the Supervisory Committee set forth in Resolution 1.

8. Resolved, That the chairmen of all divisional committees of first rank shall, before a given line of work is undertaken, notify the chairman of the Supervisory Committee of the character and scope of the contemplated work, in order that duplication by different Divisions may be avoided. In case of impending duplication and subsequent inability of the Divisions interested to come to an agreement the matter shall be decided by the Supervisory Committee.

In order to aid the chairman of the Supervisory Committee in the preparation of his annual report to the Council, the chairman of all divisional committees of first rank, and of special committees not under control of Divisions of the Society, shall each year upon call submit to him a brief report of work in progress or about to be undertaken in their respective committees.

Said chairmen shall further report to the chairman of the Supervisory Committee at the earliest possible moment the correct names of their own committees and subcommittees with a list of their members, and shall notify him of all changes made.

9. Resolved, That joint committees of this Society with other societies, shall report to the Supervisory Committee on Standard Methods of Analysis in the same way as has been prescribed in Resolutions 5 and 8 for divisional committees, and that the senior member by appointment from the American Chemical Society shall have the same rights and privileges in the Supervisory Committee as a chairman of a divisional committee.

10. Resolved, That in endeavoring to promote improvement in analytical methods the American Chemical Society does not contemplate making the use of such methods as may be recommended by its committees obligatory on any one, and, further, that no method recommended is to be considered as final, but simply as representing the best that can be done at the stated time. It is expected, as a matter of course, that revision will be exercised as knowledge and experience grow.

11. Resolved, That all previous resolutions conflicting in part or wholly with the foregoing Resolutions 1–10, are hereby repealed.

The Council voted to appoint a Committee on Chemical Museum as requested by the New York Section, and President Bancroft appointed Morris Loeb, Chairman, Victor Coblentz, Moses Gomberg, Jacob Hasslacher and Ralph H. McKee.

A letter was presented from Professor W. R. Orndorff in regard to the 60-day rule, and the Council instructed the Secretary to inform Professor Orndorff that the rule was essential to the proper conduct of the Society and could not be abrogated.

It was voted to hold the winter meeting, 1910–'11, at Minneapolis at the same time as the meeting of the American Association for the Advancement of Science.

Several invitations for the summer meeting of 1911 were presented to the Council and after careful discussion of the matter it was voted that the summer meeting for 1911 should be held in Indianapolis, the date for the same being left to the President and the Secretary with power.

The committee appointed to consider the publication of a new Journal of Agricultural and Food Chemistry reported progress and their opinion that it would not be possible to start such a journal before January, 1912. It was voted that an extension of time be granted to the committee, which would report again at the next annual meeting.

It was voted that the Council of the American Chemical Society endorsed the creation of a National Department of Health and that a committee be appointed to draw up suitable resolutions to be presented to the proper authorities. President Bancroft appointed Edw. C. Franklin, Charles F. Crowley and H. E. Barnard.

Communications were read from Mr. H. L. Taylor, of the Educational Department of New York State, in regard to the formation of a joint committee on spelling with other associations in order that greater uniformity in chemical spelling might be adopted. After discussion the Council voted that the matter be referred with power to the Board of Editors of the Journal of the American Chemical Society to confer with the committee mentioned by Mr. Taylor and to proceed as circumstances may warrant.

An application being received from twenty members in good standing, as required by the Constitution, it was voted to grant a charter to a new Section to be formed in territory within a radius of seventy miles of Pullman, Washington, said charter to become effective when a descriptive geographical name for the Section was decided upon. The Secretary was authorized to pass upon the matter for the Council.

The by-laws of the Pharmaceutical Division, passed by the Division at the Boston Meeting, were approved by the Council.

It was voted to accept the invitation of the Supervisory Board of the *American Year Book* to appoint a member of that Board representing the American Society, and the Council voted that the Secretary be designated as such.

The Council directed the Secretary to extend the thanks of the Council and the Society to the Chicago Section and the committee in charge of the entertainment at the La Salle Hotel; to the Los Angeles members through the committee appointed to represent them; to the Sierra Madre Club; to Mr. S. T. Mather and the Sterling Borax Company; to the San José Chamber of Commerce; to Ralph A. Gould, S. W. Young, Felix Lengfeld, W. C. Blasdale, F. T. Green, B. S. Drake, A. A. Hanks, Arthur Lachman and the committees of which they were chairmen; to the California Section; to P. C. Rossi, President of the Italian-Swiss Colonies; to Mr. E. B. Braden, of the Selby Smelting and Lead Company; to the Puget Sound Section and the committee representing them, for the overwhelming hospitality that has already been outlined in the general Proceedings.

By request of the President of the Second National Conservation Congress, President Bancroft has appointed to represent the American Chemical Society in that Congress: G. B. Frankforter, Marston T. Bogert, C. F. McKenna, F. G. Cottrell, W. C. Ebaugh.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary*.

MEMBERS ELECTED BETWEEN JULY 15TH AND AUGUST 15TH.

Agraz, Juan S., 6ª del Cipres 176, City of Mexico, Mexico.
Akers, Harry G., 447 Jarvis St., Toronto, Canada.
Anaconda Copper Mining Co., Anaconda, Mont.
Ball, Theodore R., 2625 Cottage Grove Ave., Des Moines, Ia.
Beifeld, Herbert A., 5172 Michigan Ave., Chicago, Ill.
Coe, J. E., 802 Ave. A, Dodge City, Kans.
Crawford, John, Jr., University Club, Portland, Ore.
Daniels, Vincent I., Box 385, Greeley, Colo.
Darling & Co., Union Stock Yards, Chicago, Ill.
Deitchman, Hyman, 2013 N. Western Ave., Chicago, Ill.
Doll, M. G., University Club, Salt Lake City, Utah.
Dunham, Gardner S., 210 Walnut Place, Syracuse, N. Y.
Dunn, Edgar M., Anaconda, Mont.
Eaton, Walter, Coram, Calif.
Elkins, A. W., 2340 Piedmont Ave., Berkeley, Calif.
Flint, Edward R., Univ. of Florida, Gainesville, Fla.
Furness, Radclyffe, c/o Midvale Steel Co., Philadelphia, Pa.
Grageroff, I., Emporium, Pa.
Gray, Carl W., 815 Park Ave., South Pasadena, Calif.
Hayward, Lawrence B., 73 Charlotte Ave., Detroit, Mich.
Irwin, W. H., 1207 N. 26th St., St. Joseph, Mo.
Johnson, Wellington B., Tabor, Ia.
Johnson, Wm. C., 10 Arlington St., South Framingham, Mass.
Junghandel, Max, Fairmont Hotel, San Francisco, Calif.
Kirby, W. E., Princeton, N. J.
Knecht, G., Mission St., San Francisco, Calif.
Levy. Nathan, 98 Morningside Ave., New York City.
MacGregor, John R., 9809 South Wood St., Chicago, Ill.
MacPherson, Roy P., Sims Hall, Syracuse, N. Y.
Mashek Chemical and Iron Co., Wells, Mich.
Maynard, Leonard, Middletown, Conn.
McNally, Wm. F., Marcellus, N. Y.
Moeller, Willy, 29 Broadway, New York City.
Moore, G. Allan, 6034 Prairie Ave., Chicago, Ill.

Morse, Irving H., 230 Terry St., Longmont, Colo.
Rouse, K. H., Cement, Calif.
Scott, James W., 711 North Sarah St., St. Louis, Mo.
Selvig, Walter, c/o International Stock Food Co., Minneapolis, Minn.
Show, John H., c/o Cudahy Packing Co., So. Omaha, Nebr.
Stalder, Walter, 1412 12th Ave., Oakland, Calif.
Taylor, Charles E., Drawer M, Penn Yan, N. Y.
Turner, Wm. D., 7752 Green St., Chicago, Ill.
Uehling, F. F., Passaic, N. J.
Wahl, Ben., c/o Detroit Sulphite Pulp & Paper Co., Detroit, Mich.
Wallin, Charles E., Pine Lake, Alberta, Canada.
Wells, Arthur E., c/o Garfield Smelter, Garfield, Utah.
Wildish, James E., Springfield, Mo.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L Parsons, Durham, N. H.]

MINNESOTA SECTION.

The 27th regular meeting was held in the Chemical Laboratory of the University of Minnesota, on Friday evening, May 20th, at 8 P.M. Committees for the meeting of the Society next winter were announced, and the following program was rendered: "The Diffusion of Oxygen Through (*a*) Organic Liquids, and (*b*) Solids." G. B. Frankforter, G. W. Walker, and R. S. Callaway. "Influence of Traces of Iron, Lead and Copper on the Color of Cadmium Sulphide," G. B. Frankforter and J. G. Dietrichson.

FRANCIS C. FRARY, *Secretary*.

PHILADELPHIA SECTION.

The regular meeting of the Section was held at the Chemical Laboratory of Swarthmore College on June 16th and was preceded by the regular dinner, served in the Library of the College. The program consisted of an address by Dr. Edgar F. Smith, of the University of Pennsylvania, on "Modern Electro-Chemical Analysis," illustrated by experiments. The attendance was unusually large.

C. S BRINTON, *Secretary*

NORTH CAROLINA SECTION.

The summer meeting of the Section was held in the Agricultural Building at Raleigh on Wednesday, June 22nd, at eleven o'clock A.M. After a brief business session the following program was presented. Report: "Colloidal Chemistry," by Duncan MacRae. "The Unsaturated Character of the Resins of *Pinus Sabiniana*," by C. H. Herty and E. N. Tillett. "The Specific Heat of Benzol and Its Saturated Vapor," by J. E. Mills and Duncan MacRae. "The Bleaching of Flour by Nitrogen Peroxide," by W. M. Allen, State Food Chemist. "The Effect of Acids on Ethyl-Phospho-Platino-Chloride," by C. H. Herty and Hampden Hill. "The

Specific Heat of Carbon Tetrachloride and Its Saturated Vapor," by J. E. Mills and Duncan MacRae. "A Study of the Resene of *Pinus Hetrophylla*," by C. H. Herty, W. A. Houck and T. P. Nash.

BURTON J. RAY, *Secretary*.

MILWAUKEE SECTION.

The annual meeting of the Section was held on June 24th, at the Hotel Blatz. There was not formal program but a "Kneippe" was held. The following officers were elected for the ensuing year: H. W. Rohde, *Chairman*; F. S. Low, *Vice-Chairman*; Ben L. Salomon, *Secretary*; E. V. Manuel, *Treasurer*; George N. Prentiss, *Councilor*.

The Milwaukee Section held an informal meeting at Whitefish Bay on August 12th. Matters of interest and the policy and welfare of the Section for the coming year were discussed.

BEN L. SALOMON, *Secretary*.

RHODE ISLAND SECTION.

The annual meeting and excursion was held on June 25th, the trip this year being to the mines of the Rhode Island Coal Co., at Portsmouth. Dinner was served upon arrival, and the mines were visited immediately after the annual meeting following the dinner.

ALBERT W. CLAFLIN. *Secretary*

Issued with the October Number, 1910.

Proceedings.

COUNCIL.

MEMBERS ELECTED BETWEEN AUGUST 15TH AND SEPTEMBER 15TH.

Alexander, James, 2208–15th St., Walbrook, Baltimore, Md.
Anderson (Mrs.), A.M., Univ. of Chicago, Chicago, Ill.
Blakstadt, Ragnvald, Stortingsgaden 10, Kristiania, Norway.
Buckborough, S. A., Evanston, Ill.
Cope, R. P., 512 W. 65th St., Chicago, Ill.
Dunbar, B. A., Lidgerwood, No. Dakota.
Green, Vennis A., 201 Iowa St., Redfield, So. Dakota.
Keiller, P. A., Colombo Commercial Co., Ltd., Colombo, Ceylon.
Kurtz, J. M., Parkside, Goshen, Ind.
Maines, Eugene L., 463 E. Gay St., Columbus, Ohio.
Nead, Walter H., 1131 N. Custer Ave., Colorado Springs, Colo.
Rittman, W. F., Planebrook, Chester Co., Pa.
Sanderson, J. McE., 2013 W. 104th St., Cleveland, Ohio.
Simkins, George, 640 Maryland Ave., Pittsburg, Pa.
Speers, J. A., Saskatoon, Saskatchewan, Canada.
Test, C. D., Golden, Colo.
Thompson, L. R., Berlin, Wis.
Timmons, G. D., Valparaiso, Ind.
Wang, Yinchang Tsenshan, Univ. of Chicago, Chicago, Ill.
Warman, A. S., 613 Greenup St., Covington, Ky.
White, George F., Richmond College, Richmond, Va.

DECEASED MEMBERS

Constantin Fahlberg, Nassau a/d Lahn, Germany.
F. A. Genth, Jr., Sept. 1st, Lansdowne, Pa.
Charles A. Goessmann, Sept. 1st, Amherst, Mass.
M. T. Jones, Jr., East Orange, N. J.
Albert E. Leach, Aug. 22nd, Denver, Colo.

George Frederic Barker.

When the writer of the following paragraphs began the study of chemistry in 1872, his text-book was an "Elementary Chemistry" then in its tenth edition, written by the subject of this article. At the time the writer never dreamed that he was to become a colleague of this distinguished scientist, nor did it occur to him for a moment that at a later period he would be called upon to write in memory of this splendid teacher, profound student, and man of noblest character.

The face of Dr. Barker was quite familiar to men of science, both in this country and abroad, as he made it a point, when at all possible, to meet together with his fellows in science, thereby endearing himself to a wide circle of sympathetic friends, who, in recent years, have keenly felt his absence from their meetings, and were, indeed, shocked when the message of his death was announced. It was my privilege to meet Dr. Barker daily for many years, not so intimately at first, but later with the greatest freedom, and in true companionship. The impression made by him, at all times, was that of an earnest student of science, thoroughly conversant with its most recent advances and able, in a marked degree, to render what ordinarily seemed dry and unattractive, but extremely important, so simple and so fascinating, that the most ordinary layman might comprehend with ease. His lectures to students were celebrated for their clarity of presentation, as well as for their wide scope. He delighted in experiments, and one of his chief joys was to illustrate his lectures, as far as possible, with an abundance of attractive and striking experiments. The most intricate topics were presented before large audiences, reaching sometimes into the thousands, concisely and clearly, and so brilliant were his successes that he became noted throughout the country as one capable of popularizing science as few could do it. The writer recalls an occasion in his younger days, when the Academy of Music in Philadelphia was filled to its dome with an intensely interested and intelligent audience assembled to listen to Dr. Barker's lecture on "Sound," and, while seated in the "sky parlor" of the immense auditorium, enjoying the discomforts peculiar to his altitude at the moment, so intensely absorbing was the lecture and its experiments that at the conclusion it was difficult for him to realize that he had actually sat there more than an hour as an auditor.

As previously remarked, Dr. Barker's interest in his fellow men won for him hosts of friends, among whom were a number of the most eminent scientists of his day. Gladly did they present him with mementoes of their friendship, which he carefully cherished and joyfully exhibited to friends and students upon all proper occasions. In all gatherings he was a central figure. His affability and his courtesy were marked characteristics.

He was most deeply esteemed in the community where he lived by persons of all ranks. For a number of years he served on the Board of Education in the city of Philadelphia, and there exerted an influence which was entirely for the good, and never to be forgotten.

As a teacher he was painstaking in the presentation of his subject. It was a matter of conscience with him to have his students grasp and understand the problems he placed before them. He would go to any trouble to make abstruse points clear, and while at times he seemed to demand almost too much and be a bit brusque, yet no earnest student was ever turned away. The sincerity of the inquirer always led him to cast aside time, labor and comfort. Indeed, he was the true teacher, whose sole object was the welfare of those whom he taught.

At various times he appeared as an expert in scientific matters, and in this field further demonstrated his spirit of careful investigation, and absolute integrity and loyalty, as well as ability to be just and fair to all. Many of the cases involved the highest scientific knowledge and accuracy, which were abundantly supplied by him.

By his colleagues in the teaching staff of the University of Pennsylvania, he was most highly esteemed. His services were constantly engaged upon committees, and those who worked with him in such duties entertained but one impression,- to wit, that he was capable of handling the most intricate and perplexing problems with fairness, calmness and the best judgment. Indeed, it was a pleasure to be associated with him in work of this description. As a younger colleague, who profited so much by association with Dr. Barker, I cheerfully record my indebtedness to him for the most hearty coöperation and for his many helpful suggestions in the solution of the problems which fell to me. Dr. Barker was absolutely free from many of the littlenesses of character which so often mar the record of men of science and scholarship. It was a pleasure to place before him any little piece of work that one might be doing, for his mind was ever alert and open to new things, while he was always ready with an encouraging word or helpful suggestion.

His early academic training was received in the Boston Public Schools, and at the Academy in South Berwick, Maine. He further served an apprenticeship with Joseph Weightman- a maker of scientific apparatus, going thence to Yale where he was assistant in chemistry before graduation from the Sheffield Scientific School of that University in the year 1858. He was deeply attached to his Alma Mater, and invariably spoke in the highest praise of his early teachers. Indeed, for some of them his regard verged upon worship. His serious student days had, however, a bit of the modern in them, for if the writer remembers correctly, he was a member of the 'Varsity crew in the year of his graduation. Some years later in the autumn of 1869 he became Professor of Physiological Chemistry and Toxicology in the Medical School. Indeed, the chair was created for him. During this period, he served as expert for the State in several poison cases, the most noted being the Lydia Sherman case in New Haven. While lending to his colleagues such assistance as was possible, he was active scientifically. Thus, the *American Journal of Science*, **43**, 252, second series, contains a brief article "Upon the Silvering of Glass," which is a modification of a suggestion of Böttger.

Again, there appeared an article entitled "Account of the Casting of a Gigantic (Rodman) Gun at Fort Pitt Foundry," *Am. J. Sci.*, **37**, 296 (1863), which is really a letter from Dr. Barker to the editors of the journal upon a topic which, at the time, was attracting much attention.

A most interesting contribution is made, in the same journal (second series, 44, 263 (1867)), by Dr. Barker in support of the view that formic acid is carbonous acid. He believed this to be true because of the ready formation of formic acid by the partial oxidation of carbon, and also because it resulted from the reduction of carbonic acid. For these reasons he further concluded that formic acid was the acid of bivalent carbon.

Shortly after he contributed an extended communication "On Normal and Derived Acids," *Am. J. Sci.*, second series, 44, 384. He endeavored in this to aid in the establishment of a rational nomenclature.

In 1870 appeared his text-book of "Elementary Chemistry, Theoretical and Inorganic," which ran through many editions as well as translations into other languages and was the first book in our language wherein modern chemistry is presented systematically. The style of the book, as so many can testify from its study, is concise and clear. Wolcott Gibbs spoke of it as "a book wholly in the spirit of the most advanced thought in the science," but it may be added that Dr. Gibbs took some exception to the nomenclature employed by Dr. Barker, for he said that "such terms as potassium chlorate, calcium phosphate, etc., ... are, to say the least, of doubtful etymological propriety, and we greatly prefer the adjective form—potassic chlorate, calcic phosphate, etc."

A translation of Meissner's "Researches upon Electrolyzed Oxygen," was published by him in the *Am. J. Sci.*, second series, 1, 213.

During his sojourn at New Haven, he contributed a note "On the Spectrum of an Aurora which Appeared at New Haven, November 9, 1871." The point of particular interest in this observation was the fact that the line of wave length, 502, was not laid down in any authority accessible to the observer, as having been noted in the aurora spectrum. He adds: "Indeed, no previous observer, so far as I know, has seen any auroral line between the Frauenhofer lines *b* and F" (*Amer. J. Sci.*, third series, 2, 465 (1871)).

Some time later, he presented a second contribution "On the Spectrum of an Aurora of October 14, 1872." This aurora, like the one observed in 1871, was distinguished by its radiant crimson color, and by its form. Dr. Barker remarks that in the lines that appeared in the spectrum, none were new, though no previous observer had seen all of them at once. Vogel had seen five, and four had been seen by Dr. Barker. Two of the lines coincided nearly with the solar lines F and G, but a considerable difference was observed between the spectrum of this aurora and that of 1871, for three lines of the aurora of 1872 had no corresponding lines in the spectrum of the aurora of 1871.

Dr. Barker was assistant to Dr. Bacon in the Harvard Medical School from 1859–1861; Professor of Chemistry in Wheaton College, Illinois, 1861; then in the Albany Medical College, where he won the degree of Doctor of Medicine (1862–1863), making while there a chemical examination of the viscera of a dead body, the first time this had ever been done in this country; next, in the University of Pittsburg (1863); he also delivered the lectures on chemistry at Williams College in the years 1868 and 1869, and after service in his Alma Mater, to which reference has already been made, he became Professor of Physics in the University of Pennsylvania (1872) where the remainder of his life was spent. At this period he published a contribution of considerable length, with illustrations, on "A New Vertical Lantern Galvanometer," in which claim is made for the general principles of construction of the instrument, and the advantages possessed by it in the readiness with which it could be put into use, the brilliancy of the illuminated circle of light which it gave upon the screen, its great range of delicacy by which all experimental requirements might be answered, and, finally, the satisfactory character of its performance as a demonstration galvanometer (*Proc. Amer. Phil. Soc.*, **14**, 440).

This was followed by a communication "On the Measurement of Electromotive Force" (*Proc. Amer. Phil. Soc.*, **20**, 649) in which he described a form of Daniel cell in which the zinc sulphate and copper sulphate solutions were kept separate by closing a stopcock when the cell was not in use.

In 1880, before the American Association for the Advancement of Science, at its Boston meeting, Dr. Barker, as retiring president, delivered an address upon "Some Modern Aspects of the Life-Question."

In following the career of our friend there is plainly seen a versatility on his part, as well as a keen interest for other branches of science than that one to which he gave the best years of his life. Thus, he is found a member of an expedition to Rawlings, Wyoming, for the purpose of reporting "On the Total Solar Eclipse of July 29, 1878." His particular duty was to observe with an analyzing spectroscope the presence, either, of light or of dark (Fraeunhofer) lines in the spectrum of the corona.

Again, in connection with Professor Rowland, he reported "On the Efficiency of Edison's Electric Light" (*Am. J. Sci.*, third series, **19**, 337). Dr. Barker was the first to exhibit radium in this country (1899), after its isolation by Madam Curie in Paris, and radioactivity appealed so strongly to him, that it is not surprising to find "Radioactivity of Thorium Minerals" in the *Am. J. Sci.*, fourth series, **16**, 161. In this communication, the author introduces a number of original observations.

A very instructive address upon "Radioactivity in Chemistry" was delivered by Dr. Barker before the Chemical Society of Columbia University. It appeared in full in the *School of Mines Quarterly*, **24**, 267. It has historical value, and will prove extremely helpful to all wishing to familiarize themselves with the subject. It is accompanied with bibliographies covering 90 titles by the most prominent investigators in this particular field of research.

In 1899, Harper and Bros. issued a small volume of 75 octavo pages on "Röntgen Rays" in which are incorporated memoirs by Röntgen, Stokes, and J. J. Thompson, translated and edited by Dr. Barker.

On the 27th of May, 1893, the American Philosophical Society celebrated the 150th anniversary of its foundation, on which occasion Dr. Barker offered a paper on "Electrical Progress since 1743." This paper is a review of the advances in electricity, since that early date, emphasizing in particular the contributions to electrical science by such persons as the immortal founder of the Society, Benjamin Franklin, and by Kinnersley, Robert Hare, Joseph Henry, Joseph Saxton, David Rittenhouse and Alexander D. Bache. "The labors of these men have mightily contributed to advance the development of scientific thought throughout the world, and so to bring about that exceptional evolution of electrical facts and theories which is the distinguishing feature of the science of the nineteenth century. This little brochure is indeed worthy of study by every student of the physical sciences. It contains an appendix showing a list of ninety-three papers on "Electricity and Magnetism," published by the American Philosophical Society.

Still other communications of Dr. Barker are "On the Henry Draper Memorial Photographs of Stellar Spectra (*Am. Phil. Soc.*, **24**, 166); "On the Use of Carbon Bisulphide in Prisms" (*Am. J. Sci.*, third series, **29**, 269), in which article there is presented to the public the observations of his friend, Dr. Henry Draper, taken from the notes of the latter after his death; and "The Microphone of Hughes" (*Am. J. Sci.*, third series, **16**, 60), in which Dr. Barker takes occasion to say that the results obtained by Hughes had been clearly anticipated by more than a year by those of Edison. His argument, throughout, is in support of Edison's apparatus, and there is frequent demonstration of its superiority over that of Hughes.

Biographical memoirs of Frederick Augustus Genth, of Henry Draper, of John William Draper, and of M. Carey Lea were written for the National Academy by Dr. Barker, and he also prepared for the Smithsonian Institution annual reports upon physics from the year 1881 to 1885, inclusive. These amount to 253 pages and represent the most recent advances in the science during these years.

From 1868–1900 he was Assistant Editor of the *American Journal of Science*. In 1874–75 he was Editor of the *Journal of the Franklin Institute.*

In 1892 appeared his "Physics, Advanced Course" from the press of Henry Holt and Company, which immediately met with a most hearty reception and became a standard among the text-books on this most important subject.

It follows naturally that to one so active in the scientific world, there should be awarded numerous honors. Thus, in 1881, Dr. Barker was United States Commissioner to the Paris Electrical Exhibit, a delegate to the Electrical Congress, and Vice-President of the Jury of Awards, receiving the decoration of Commander of the Legion of Honor in France; in 1884, he was United States Commissioner to the Electrical Exhibit in Philadelphia; and in 1893, a member of the Jury of Awards of the World's Columbian Exposition. He was an active member of the National Academy of Sciences, serving on many of its important committees, and also of the American Association for the Advancement of Science, of which he was Vice-President twice, delivering on one of these occasions an address on "The Molecule and the Atom," a most valuable contribution to theoretical chemistry, and President in 1879. He was a corresponding member of the British Association. He was President of the American Chemical Society (1891), the subject of his presidential address being "The Borderland between Physics and Chemistry." He was secretary and later a vice-president of the American Philosophical Society from 1899 until 1909. He was a member of the Physical Society and of the Deutsche chemische Gesellschaft. In 1899 he became an honorary member of the Royal Institute of Great Britain.

He was the recipient of the following academic honors: Doctor of Science from the University of Pennsylvania in 1898; LL.D. from Allegheny College in 1898; and LL.D. from McGill University in 1900.

He became Emeritus Professor of Physics in the University of Pennsylvania in 1900. He was a member of the Century Club of New York and of the University Club of Washington.

In 1861, Dr. Barker was married to Mary M. Treadway, of New Haven, Conn., who, with three daughters, survives this devoted and loving husband and father.

Dr. Barker was born at Charlestown, Mass., July 14, 1835, and died at Philadelphia upon May 24, 1910.

His was a beautiful life, so full of service to his fellow men and so rich in its achievements, that it will ever remain a most precious memory to his many friends.

EDGAR F. SMITH.

WILLARD GIBBS MEDAL.

Owing to the generosity of Mr. W. A. Converse the Chicago Section has established a Gold Medal known as the Willard Gibbs Medal to be awarded annually according to the following regulations transmitted by A. L. Nehls secretary.

RULES FOR THE AWARD OF THE WILLARD GIBBS MEDAL FOUNDED BY WM. A. CONVERSE.

I. A GOLD MEDAL shall be awarded annually for the best paper or address presented before the Chicago Section of the AMERICAN CHEMICAL SOCIETY, provided it be of sufficient merit. This medal shall be known as the WILLARD GIBBS MEDAL, founded by Wm. A. Converse. The award may be made to any one, *provided* he be a member of the AMERICAN CHEMICAL SOCIETY at the time the paper or address was delivered, and provided it is eligible under the following conditions:

(*a*) The Medal shall be awarded at the November meeting of the Chicago Section for a paper or address delivered before the Section between September 1st of the previous year and July 1st of the year of the award. The first medal shall be awarded in November, 1911.

(*b*) The paper or address shall be complete in itself, shall be presented by the author, and shall not have been read or published previously. To be considered for the award a typewritten copy of the paper or address shall be submitted to the jury, through the Chairman of the Section.

(*c*) It is desired that the paper or address, if suitable, be published in one of the publications of the AMERICAN CHEMICAL SOCIETY.

II. The jury to determine the award of the Medal shall consist of the Chairman of the Chicago Section at the time the award is made, who shall, *ex-officio*, be Chairman of the Jury, and four other members of the Section duly elected by it.

III. The Executive Committee of the Chicago Section shall have the power to decide any question not specifically covered by these rules.

IV. The Chicago Section shall have the power to change or amend these rules under the same conditions and in the same manner as the by-laws of the Section.

Issued with the November Number, 1910.

Proceedings.

DIVISION OF AGRICULTURAL AND FOOD CHEMISTRY.

Mr. H. E. Barnard, Food and Drug Commissioner and State Chemist of Indiana, has been elected by the Executive Committee to fill out the unexpired term of Chairman C. D. Woods, resigned.

B. E. Curry, *Secretary.*

COUNCIL.

Members Elected between September 15th and October 15th, 1910.

Ashley, Myron B., Mancelona, Mich.
Avon, Hans, Philippine Medical School, Manila, P. I.
Barbey, Jacob W., 1180 Jos. Campan Ave., Detroit, Mich.
Burleson, H. L., Belvedere, Calif.
Chase, A. Nelson, Barksdale, Wis.
Gaff, Thomas T., 1520 20th St., Washington, D. C.
Gardner, Daniel, Institute of Emperor Nicholas I, St. Petersburg, Russia.
Grab, Eugene G., Custom House, Nashville, Tenn.
Hawkes, Frank E., So. Framingham, Mass.
Hogg, Elton M., Saratoga, Calif.
Higgins, Wilton A., Shawinigan Falls, Que., Canada.
Holden, R. F., 2322 So. Compton Ave., St. Louis, Mo.
Jacobs, Paul Burke, Thomas, W. Virginia.
James Pyle & Sons, Edgewater, N. J.
Johnson, Harold S., 3359 Wabash Ave., Chicago, Ill.
Loomis, Howard, Brookings, So. Dakota.
Malowan, G., 515 North Clark St., Chicago, Ill.
Moe, J. A., 528 E. Clay St., Portland, O.
Morris, Clinton, Goodrich, Tenn.
Neff, Byron D., Indianapolis, Ind.
Noble, Edward W., Winston-Salem, No. Car.
Peterson, Andrew P., 1728 4th St., S. E., Minneapolis, Minn.
Pullar, H. B., 7323 Woodlawn Ave., Chicago, Ill.
Robinson, Samuel R., 1055 Dillon Ave., Coraopolis, Pa.
Rogers, L. Joslyn, 381 College St., Toronto, Ont., Canada.
Stacy, E. E., Tuscola, Ill.
Sydnor, Leslie W., Carbon, West Virginia.
Terry, Ethel M., 6042 Engleside Ave., Chicago, Ill.
Traut, Carl E., 86 Cherry St., Battle Creek, Mich.
Tritsch, Dr. Walter, c/o Tungsten Lamp Co., Hamilton, Ont., Canada.
Weaver, Elmer R., Raisin, Calif.
Whittaker, H. A., Lab'y Minn. State Board of Health, Minneapolis, Minn.

BOARD OF DIRECTORS.

The Directors of the American Chemical Society met at 3.00 P.M., October 8th, at the Chemists' Club, New York City. All members present.

It was voted that beginning with the January number, 1911, of the *Journal of Industrial and Engineering Chemistry*, the body of the journal be printed in nine (9) point type, and that notes, patents, etc., in the end of the *Journal* be continued in eight (8) point type as heretofore.

It was voted to transfer $550.00 from General Meetings' account, and credit $400.00 to back number account and $150.00 to Secretary's expense account.

Mr. Harvey F. Mack was appointed advertising agent for the journals of the Society, and the officers of the Society were authorized to sign a contract with him, details of which were carefully considered and approved by the Directors.

It was voted that the existing rates of advertisements be approved, and that the advertising agent be allowed to give 10 per cent. discount to publishers who advertise in our journals and 2 per cent. to any advertiser for cash.

It was voted that hereafter free advertisements allowed to members seeking employment be limited to ¾ in. space and two insertions, and that extra space or extra insertions be paid for at regular advertising rates.

It was voted that $400.00 additional be appropriated to Abstractors' account of *Chemical Abstracts*.

The meeting then adjourned.

CHARLES L. PARSONS, *Secretary*.

MEETINGS OF THE SECTIONS.

[Full accounts of all meetings should be sent to Secretary Charles L. Parsons, Durham, N. H.]

CHICAGO SECTION.

The September meeting was held at the City Club, Friday, September 23rd.

The program for the evening was "Milk:" (1) "Toxicity of Milk and Milk Serum," Dr. Edward Gudeman; (2) "Cost of Production of Milk," J. P. Grier, Secretary Chicago Milk Producers' Association; (3) "Cost of Distribution of Milk," Dr. H. R. Ryder, Borden's Condensed Milk Co.; (4) "Condition of the Chicago Milk Supply," D. T. Gunning, Assistant State Chemist.

The discussion was led by J. B. Newman, Assistant State Food and Dairy Commissioner.

Members of the Section held the usual informal dinner before the meeting.

A. L. NEHLS, *Secretary*.

SECTION OF EASTERN NEW YORK.

The September meeting was held in the Union College Chemical Lecture Room, Friday evening, Sept. 23rd, at 8 o'clock. The following program was presented:

I. A. R. I. 75.

IMPERIAL AGRICULTURAL RESEARCH
INSTITUTE LIBRARY
NEW DELHI.

Date of issue.	Date of issue	Date of issue.